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A POLYSACCHARIDE FROM THE BLUE-GREEN ALGA, *ANABAENA CYLINDRICA*[1]

BY C. T. BISHOP, G. A. ADAMS, AND E. O. HUGHES

ABSTRACT

A complex polysaccharide has been isolated from the fresh-water alga, *Anabaena cylindrica*, grown in a synthetic culture medium. Prolonged acid hydrolysis yielded glucose, xylose, glucuronic acid, galactose, rhamnose, and arabinose in a molar ratio of 5 : 4 : 4 : 1 : 1 : 1. Chemical fractionations of the polysaccharide material from solution in cupriethylenediamine, and of its acetate from organic solvents indicated chemical homogeneity.

Except for the work of Hough, Jones, and Wadman (5) on *Oscillatoria* and *Nostoc*, little is known of the carbohydrate constituents of blue-green algae. In the gelatinous nodules of *Nostoc*, these authors found a complex polysaccharide containing six different sugars. The observation in this laboratory of agar-like gels formed by old partly evaporated cultures of *Anabaena*, a genus closely related to *Nostoc*, suggested that a similar carbohydrate might be present. Preliminary examination of this material showed that six sugars were present and further study indicated that they were components of one complex polysaccharide. In a recent study, Fogg (3) has described the production of a polypeptide and a pentose by the same organism. The present paper reports the properties and composition of its polysaccharide component.

Anabaena cylindrica Lemm. (Class Myxophyceae; Order Nostocales; Family, Nostocaceae) was grown in a liquid inorganic medium with or without supplementary carbon dioxide and under low or high light intensity. The same polysaccharide was found under all four conditions of growth.

The polysaccharide was isolated from the cultures after removal of non-carbohydrate material by treatment with hot dilute alkali. Examination of the acid-hydrolysis products of the polysaccharide material by qualitative and quantitative paper chromatography showed glucose, xylose, galactose, rhamnose, and arabinose in approximate molar ratios of 5 : 4 : 1 : 1 : 1. Thermal decarboxylation (10) indicated the presence of 4 moles of uronic acid. The five neutral sugars were identified by their optical rotations and by isolation of crystalline specimens. When examined on paper chromatograms the uronic acid and its methyl ester gave spots corresponding to glucurone and glucuronic

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acid methyl ester. Thus the uronic acid was tentatively identified as glucuronic acid.

Chemical fractionations of the polysaccharide material from cupriethylenediamine, and of its acetate from organic solvents, yielded no chemically different portions. Stepwise acidification of a cupriethylenediamine solution of the polysaccharide yielded four fractions with the same composition and optical rotation ($[\alpha]_D^{23}$ $-12°$). The acetate was insoluble in all organic solvents except dioxane in which it was soluble to the extent of only 0.1%. The soluble and insoluble fractions had the same compositions as the original acetate. Graded hydrolysis revealed no structural characteristics of the polysaccharide. Three hours' heating with 0.025 *N* sulphuric acid partially liberated all six components while more dilute acid had no effect.

From the evidence obtained it appears that the polysaccharide produced by *Anabaena cylindrica* is a complex, chemically homogeneous polysaccharide. Any fractionation obtained must have been on a basis of molecular weight. No confirmation of this possibility could be made because of the insolubility of all fractions in solvents suitable for molecular weight estimation.

The chemical composition of the *Anabaena* polysaccharide appeared to be similar to that of the complex acidic polysaccharide isolated from *Nostoc* by Hough *et al.* (5). The monosaccharide units, glucose, galactose, xylose, rhamnose, and glucuronic acid were present in each and, in addition, the polysaccharide of *Anabaena* contained arabinose while that of *Nostoc* contained galacturonic acid and an unknown sugar. Both polysaccharides showed a marked resistance to acid hydrolysis. Poor solubility properties and gel formation made purification difficult.

When the cell-free medium and cellular residue of *Anabaena* cultures were examined separately, polysaccharide material having the same chemical composition was found in each portion. Microscopic examination of the alga mounted in India ink showed that many of the filaments were enclosed in a mucilaginous material which was readily sloughed off into the medium. These observations suggest that the polysaccharide may be derived from the mucilaginous envelopes surrounding the trichomes.

EXPERIMENTAL

Paper strip chromatograms were run at room temperature (22–26°C.) on Whatman No. 1 using the following solvent systems: (*a*) pyridine : ethyl acetate : water, 1 : 2 : 2 (7); (*b*) butanol : pyridine : water, 6 : 4 : 3 (6); (*c*) butanol : pyridine : water, 10 : 3 : 3 (8).

Culturing of Anabaena cylindrica

A stock culture of *Anabaena cylindrica* Lemm. 1403–2 was obtained from the Cambridge Culture Collection of Algae and Protozoa.

Transfers were made to modified Chu No. 10 Solution (2) with nitrate concentration doubled and 1 ml. 4% Hoagland's solution added per liter. Presterilization pH was adjusted to 9.0 with dilute sodium hydroxide. Cultures were grown on a shaker under fluorescent daylight lamps (100–125 ft. candles)

at 28°C. Although most of the material examined was grown under the above conditions, some cultures were supplied with 6% carbon dioxide in air (about 30 ml. per min. per liter) and others exposed to a higher light intensity (900 ft. candles) with or without supplementary carbon dioxide. For cultures on which yields are reported a 100 ml. suspension of *Anabaena* (dry weight of cells, about 1.4 mgm.) was used to inoculate each 900 ml. of medium in a 2 liter Erlenmeyer flask. Dry weights were determined periodically on cellular residues and supernatants obtained by centrifuging 50 ml. aliquots at 27,000 r.p.m. for 10 min. Cellular residues and supernatants were evaporated to dryness under reduced pressure at 40°C.

At low light intensity no significant difference was found in the total dry weight yields (*ca.* 110 mgm. per 100 ml.) of eight-week-old cultures with or without added carbon dioxide. At high light intensity, cultures with or without added carbon dioxide became yellowish-brown in a few days and the experiment was discontinued in two weeks. At this time, however, dry weight yields from the carbon dioxide cultures (113 mgm. per 100 ml.) were already equivalent to those obtained in eight weeks at low light intensity and almost twice as high as those obtained from the controls (61 mgm. per 100 ml.). At both light intensities, the percentage dry weight contributed by the cellular residue was much greater in the carbon dioxide cultures (45–70%) than in the controls (10–30%).

Isolation of Polysaccharide Material

In a typical experiment a culture of *Anabaena cylindrica* was made alkaline by addition of solid sodium hydroxide to a concentration of 4%. The mixture was boiled under reflux for six hours, filtered through sintered glass, acidified (pH 4) with hydrochloric acid, and dialyzed in cellophane bags against distilled water for three days. The non-dialyzable material was isolated by freeze drying. The cream-colored product (2.39 gm. from 16 liters of a seven-week-old culture) contained 10% ash, 0.27% nitrogen, and was insoluble in water or strong alkali. Hydrolysis of a small amount (10 mgm.), by heating with 2.5% sulphuric acid (5 ml.), and examination of the hydrolyzate by paper strip chomatography (solvents (*a*), (*b*), and (*c*)) indicated the presence of rhamnose, xylose, arabinose, glucose, galactose, and an uronic acid. In a separate experiment a culture of *A. cylindrica* was centrifuged to separate cells from medium. The polysaccharide materials, isolated from both the cells and the medium, were examined by hydrolysis and paper chromatography as just described. Both materials contained the same sugars in approximately the same proportions. The same polysaccharide was found in cultures grown at low and high light intensities and with or without added carbon dioxide.

Quantitative Estimation of Component Sugars

Preliminary experiments using different acid strengths showed that the polysaccharide was very resistant to acid hydrolysis as indicated by changes in reducing power. A sample (50 mgm.) of the polysaccharide material was hydrolyzed by heating at 97°C. for 24 hr. with 2.5% sulphuric acid (10 ml.). The hydrolyzate was neutralized with barium carbonate, filtered, and individual

sugars in the filtrate were estimated by quantitative paper strip chromatography using solvent (*a*) and the phenol – sulphuric acid method of Dubois *et al.* (1). Uronic acid in the original polysaccharide was estimated by thermal decarboxylation (10). Calculated on a mole per cent basis the results showed the polysaccharide to be composed of five parts glucose, four parts each of uronic acid and xylose, and one part each of galactose, rhamnose, and arabinose. These figures are regarded as only approximate because the drastic conditions required for hydrolysis would almost certainly lead to some destruction of the sugars, particularly the pentoses.

Identification of Component Sugars

The hydrolyzate of 1 gm. of polysaccharide material was neutralized with Dowex-2 (carbonate form) and the filtrate evaporated to a syrup which was fractionated on a cellulose column (4) using butanol saturated with water as the mobile phase. The eluate from the column was collected in 5 ml. portions by an automatic fraction collector which changed the receiver every half hour. Every fifth fraction was examined by paper strip chromatography (solvent (*a*)) and appropriate portions of the eluate were combined to yield pure samples of the following sugars which were crystallized from methanol:

	m.p.		
L-Rhamnose	91– 92°C.	$[\alpha]_D^{25}$ + 8.58	(*c*, 1.4% in water)
D-Xylose	144–145°C.	$[\alpha]_D^{25}$ + 18.2	(*c*, 0.8% in water)
L-Arabinose	159–160°C.	$[\alpha]_D^{25}$ +101.0	(*c*, 1.4% in water)
D-Glucose	145-146°C.	$[\alpha]_D^{25}$ + 50.1	(*c*, 0.7% in water)
D-Galactose	170–171°C.	$[\alpha]_D^{25}$ + 78.4	(*c*, 1.27% in water)

Examination of Uronic Acid

No uronic acid could be recovered from the Dowex-2 used to neutralize the polysaccharide hydrolyzate. The hydrochloric acid hydrolyzate of 250 mgm. of the polysaccharide was neutralized with silver carbonate and excess silver ion was removed with hydrogen sulphide. The silver-free filtrate was evaporated to a syrup which was taken up in hot methanol and filtered. Paper strip chromatography of this solution (solvent (*a*)) showed the five sugars identified above and two other spots, one corresponding to glucuronic or galacturonic acid, the other corresponding to glucurone which is always associated with glucuronic acid (9).

The methanolic solution of the hydrolyzate was neutralized with ethereal diazomethane and the neutral solution was evaporated to a thin syrup. After paper strip chromatography of this syrup in solvent (*a*) for seven hours there was a spot having the same R_f value as glucuronic acid methyl ester (R_f 0.813) and situated between two spots given by galacturonic acid methyl ester (R_f 0.723, 0.833).

Attempted Fractionation from Cupriethylenediamine

The polysaccharide material (1.02 gm.) was dissolved in freshly filtered 1.0 *M* cupriethylenediamine (100 ml.) and fractionally precipitated by stepwise acidification with concentrated hydrochloric acid. Fractions were obtained at

pH values of 8.9 (0.241 gm.), 5.2 (0.012 gm.), and 4.5 (0.480 gm.). A fourth fraction (0.140 gm.), soluble in the final acid solution, was isolated by alcohol precipitation after removal of inorganic ions by dialysis. By prolonged (48 hr.) shaking it was possible to obtain 1% solutions of the above fractions in 5% sodium hydroxide. Optical rotations of these solutions were the same, $[\alpha]_D^{23} = -12.0 \pm 1°$. Samples from each fraction were hydrolyzed by heating at 97°C. for 24 hr. with 2.5% sulphuric acid. Paper strip chromatograms (solvent (*a*)) of the neutralized hydrolyzates were identical with those obtained from hydrolyzates of the original polysaccharide material.

Acetylation and Attempted Fractionation

The polysaccharide material (0.500 gm.) was added in small quantities, with stirring, to 10 ml. of formamide. The mixture was heated at 65°C. for one hour, pyridine (10 ml.) was added, and the mixture kept at 65°C. for a further 15 min. Acetic anhydride (3.2 ml.) was added in 1/4 portions to the cooled mixture which was then stirred at room temperature for 18 hr. The reaction mixture was poured with stirring into ice water (200 ml.) and the precipitate, removed by centrifuging, was washed three times with water before it was dried *in vacuo* over phosphoric anhydride. After another acetylation by the same procedure the acetate was obtained as a white powder (0.407 gm.), insoluble in chloroform, acetone, or pyridine and only 0.1% soluble in dioxane. This solution gave no optical rotation, undoubtedly because of the low concentration. The portions of the acetate soluble and insoluble in dioxane were separately deacetylated by 4% alcoholic sodium hydroxide, and hydrolyzed with 2.5% sulphuric acid. Paper strip chromatograms (solvent (*a*)) of the neutralized hydrolyzates were identical with those given by hydrolyzates of the original polysaccharide material.

Graded Hydrolysis

Samples (50 mgm.) of the polysaccharide material were heated separately at 97°C. with 5 ml. of each of the following acid solutions: 0.02 *N* oxalic, 0.02 *N* sulphuric, and 0.025 *N* sulphuric. At one hour intervals samples were removed for examination by paper strip chromatography. Neither 0.02 *N* oxalic or 0.02 *N* sulphuric acid had any effect on the polysaccharide in seven hours. Three hours' heating with 0.025 *N* sulphuric acid released small amounts of all six component sugars. Complete hydrolysis of the polysaccharide, as determined by reducing power, required more drastic hydrolytic conditions (2.5% sulphuric acid, 97°C. for 24 hr.).

ACKNOWLEDGMENTS

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REARRANGEMENT STUDIES WITH C^{14}

II. THE PREPARATION OF 2-PHENYLETHYL HALIDES[1]

By C. C. Lee and J. W. T. Spinks

ABSTRACT

The 2-phenylethyl halides were prepared from the treatment of 2-phenylethanol-1-C^{14} with thionyl chloride alone, thionyl chloride in pyridine, 48% hydrobromic acid, 55% hydroiodic acid, or phosphorus and iodine. Except for the reaction with thionyl chloride in pyridine, these reactions gave rise to some rearrangement of the C^{14} activity from the C-1 to the C-2 position. It appears probable that these rearrangements resulted from reactions having the S_N1 type of mechanism with the phenylethyl cation as reaction intermediate. The fact that the thionyl chloride in pyridine treatment leads to a product without rearrangement is of interest in that this method may have further applications in synthetic tracer chemistry.

INTRODUCTION

Among the most common methods for the preparation of an alkyl halide is the replacement of the hydroxyl group of an alcohol by a halogen through the reaction of the alcohol with a hydrohalic acid or a halide of sulphur or phosphorus. That the mechanism of such a replacement reaction may be bimolecular involving Walden inversion (S_N2) or unimolecular with a carbonium ion as intermediate (S_N1) has been pointed out by Hughes, Ingold, and co-workers (1). If the S_N1 mechanism were involved, typical carbonium ion-type rearrangements (2*b*) would be observed if conditions were favorable for rearrangement. For example, extensive structural changes occurred when pinacolyl alcohol was treated with hydrochloric acid (15) while less pronounced rearrangements were observed when *n*-amyl alcohol or pentanol-2 were heated with $ZnCl_2$ and HCl (13, 14).

It has previously been pointed out that the use of C^{14} as a tracer makes possible studies of rearrangements otherwise unobservable (5). In an attempt to convert cyclopentanol-1-C^{14} to cyclopentyl bromide with phosphorus tribromide, Loftfield (6) found that 20% of the total radioactivity had become rearranged to positions other than C-1. He pointed out that this reaction likely involved a carbonium ion "sufficiently free" to permit a "hydride ion" migration. On the other hand, Roberts *et al.* (10) observed no rearrangement of the C^{14} activity when 2-methyl-2-propanol-2-C^{14}, 2-methyl-2-butanol-1-C^{14}, and 2-methyl-2-butanol-2-C^{14} were converted to the corresponding chlorides by treatment with concentrated hydrochloric acid. In these cases, rearrangement of the C^{14} activity is unlikely because it would require the transformation of tertiary carbonium ions to the energetically less favorable secondary and/or primary carbonium ions. In the present paper, rearrangements observed in the preparation of 2-phenylethyl halides from the reaction between 2-phenylethanol-1-C^{14} and thionyl chloride, hydrobromic acid, hydroiodic acid, or phosphorus and iodine are reported.

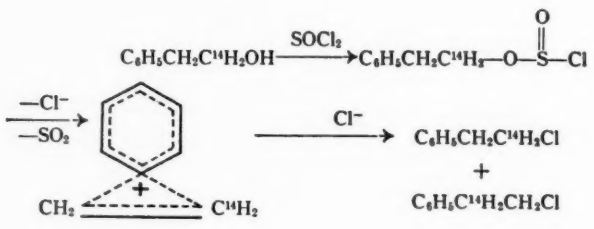
[1]*Manuscript received May 27, 1954.*
Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Sask.
For Paper I, see Reference 5.

RESULTS AND DISCUSSION

The degrees of rearrangement in the various preparations of 2-phenylethyl halides studied are summarized in Table I. The labeled 2-phenylethanol was synthesized by the lithium aluminum hydride reduction of phenylacetic acid carboxyl-C^{14} (8) obtained from carbonation, with $C^{14}O_2$, of the corresponding Grignard (5). That all the radioactivity was in the C-1 position was shown by oxidation of the labeled alcohol to non-radioactive benzoic acid. All the samples of 2-phenylethyl halides obtained were treated with magnesium in dry ether and then reacted with dry ice to give crystalline hydrocinnamic acid for radioactivity determination.

Subsequent oxidation of the hydrocinnamic acid to benzoic acid and measurement of its activity gave the amount of rearrangement from the C-1 to the C-2 position. It may be noted that the direct oxidation of the 2-phenylethyl halides to benzoic acid is also possible. Trials with inactive materials, however, showed that the conditions required to effect such an oxidation are quite drastic, and the yields attainable are low compared to that obtained from the oxidation of hydrocinnamic acid. Consequently, only one active sample of 2-phenylethyl iodide was oxidized directly, and the degree of rearrangement observed agreed very well with that found by the oxidation of hydrocinnamic acid derived from the same sample.

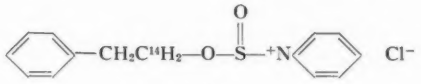
Except for the reaction of 2-phenylethanol-1-C^{14} with thionyl chloride in pyridine, all reactions studied gave rise to some rearrangement of the C^{14} activity from the C-1 to the C-2 position. Most probably, these rearrangements resulted from reactions having the S_N1 type of mechanism with the phenylethyl cation as reaction intermediate. The possible nature of the phenylethyl cation and how it might cause the rearrangement of C^{14} from C-1 to C-2 has previously been discussed (5, 11). It is noteworthy that in the treatment of the labeled alcohol with thionyl chloride alone, the resulting 2-phenylethyl chloride has its C^{14} activity practically equally distributed in the C-1 and C-2 positions. Such a finding is as would be expected if the phenylethyl cation has the symmetrical "non-classical" structure I.



I

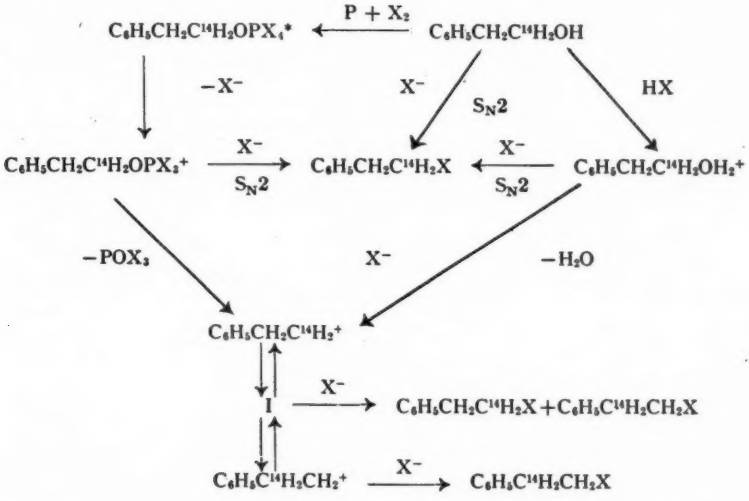
When the reaction with thionyl chloride is carried out in pyridine, a pyridinium chloride complex, II, (4) may be formed which, on decomposition, gives 2-phenylethyl-1-C^{14} chloride without rearrangement since no carbonium

ion intermediate is likely to be formed with the organic base, pyridine, as solvent.



II

The degree of rearrangement found in the 2-phenylethyl bromide or iodide prepared from the treatment of the labeled alcohol with 48% hydrobromic acid, 55% hydroiodic acid, or phosphorus and iodine ranged from 2.5 to 7.4%. (Table I). In these instances, only a fraction of the reaction proceeds through the unimolecular mechanism involving rearrangement of the intermediate phenylethyl cation. The major portion of the reaction follows a process or processes which lead to no rearrangement. Such a process may be of the S_N2 type, or it may involve the rapid interaction between the unrearranged phenylethyl cation and the conjugate base of the reaction medium as previously suggested (5, 11).



It is of interest to note that the reaction of 2-phenylethanol-1-C^{14} with hydrobromic acid resulted in a greater degree of rearrangement than the corresponding reaction of the labeled alcohol with hydroiodic acid. Apparently the protonating power of 48% hydrobromic acid, as measured by Hammett's acidity function, H_0 (2*a*), is greater than that of 55% hydroiodic acid. That such a deduction is a reasonable one is further supported by the fact that the electron affinity of bromine is greater than that of iodine (9).

**Complex $ROPX_4$ has been suggested by Kenyon and co-workers (4) as intermediate in the reaction between ROH and PX_5. No attempt was made in the present study to definitely establish the structure of complex $C_6H_5CH_2CH_2OPX_4$. Another possible intermediate may be $C_6H_5CH_2CH_2OPX_2$.*

In view of the finding that the reagents frequently employed for the preparation of alkyl halides may give rise to rearranged products, it is of utmost importance that in the syntheses of C^{14}-labeled compounds, whenever the use of alkyl halides is involved, the positions of the labeled atoms in the final products be unequivocally established. In order to obtain a cyclopentyl-1-C^{14} halide for further synthetic applications, Loftfield (6) prepared the *p*-bromobenzenesulphonate of cyclopentanol-1-C^{14} and then treated this sulphonate with sodium iodide in acetone, a typical S_N2 reaction, to give the iodide without rearrangement. The observation that the replacement of a hydroxyl group with chlorine effected by thionyl chloride in pyridine eliminated the possibility of rearrangement (14) is here extended and shown to be applicable for C^{14}-labeled 2-phenylethanol. It is our belief that the thionyl chloride in pyridine method is much less time consuming and likely to give higher over-all yields than the sulphonate – sodium iodide in acetone method for the preparation of unrearranged alkyl halides, though both of these methods will most likely find further applications in the syntheses of C^{14}-labeled compounds.

TABLE I

REARRANGEMENTS IN 2-PHENYLETHYL HALIDES FROM 2-PHENYLETHANOL-1-C^{14}

Reagents used	Compound counted†	Specific activity, counts/min./mM. Run I	Run II	% rearrangement Run I	Run II
	Phenylurethan of 2-phenylethanol-1-C^{14}	1133 ±16			
	Benzoic acid‡	0.6± 3.6		0.0	
$SOCl_2$ alone	Hydrocinnamic acid	902 ±12	1134 ±13		
	Benzoic acid	453 ± 7	551 ±10	50.3	48.6
$SOCl_2$ in pyridine	Hydrocinnamic acid	1152 ±14	1132 ±13		
	Benzoic acid	−0.1± 3.2	−0.2± 3.2	0.0	0.0
48% HBr	Hydrocinnamic acid	1170 ±14	1143 ±13		
	Benzoic acid	82.0± 3.2	60.6± 2.5	7.0	5.3
55% HI	Hydrocinnamic acid	1158 ±13	1190 ±14		
	Benzoic acid	28.3± 2.5	32.7± 3.0	2.5	2.7
	Benzoic acid§	32.3± 3.0		2.8	
$P+I_2$	Hydrocinnamic acid	702 ±10	715 ±10		
	Benzoic acid	38.3± 3.6	531 ± 4.5	5.5	7.4

†*As "infinitely thick" samples of constant geometry in a windowless Q-gas counter.*
‡*From oxidation of 2-phenylethanol-1-C^{14}.*
§*From direct oxidation of active 2-phenylethyl iodide.*

EXPERIMENTAL

Reaction with Thionyl Chloride

In a 100 ml. round-bottomed flask, cooled in an ice bath and fitted with a reflux condenser, was placed 5.00 gm. of 2-phenylethanol-1-C^{14}. Fifteen milliliters of thionyl chloride was added slowly. The mixture was removed

from the ice bath and refluxed gently for one half hour. The excess thionyl chloride was distilled off and the residue fractionated under reduced pressure. The yields of 2-phenylethyl chloride, b.p. 85–87°C. at 17 mm. (lit.(16) b.p. 81–84°C. at 14 mm.), for the duplicate runs were 4.64 and 4.40 gm. (81 and 77%, respectively).

Reaction with Thionyl Chloride in Pyridine

To a solution of 5.00 gm. of 2-phenylethanol-1-C^{14} in 20 ml. of pyridine in a 250 ml. Erlenmeyer flask cooled in an ice-bath was added portionwise 10 ml. of thionyl chloride. When the mixture was shaken and then heated on a steam bath for about five minutes (prolonged heating will cause extensive decomposition) a black solution resulted. The mixture was then allowed to stand at room temperature for one half hour before it was poured into ice water. The product was extracted with ether, the extract being washed successively with distilled water, dilute hydrochloric acid, 10% sodium bicarbonate solution, and distilled water. After the extract was dried over anhydrous sodium sulphate, the ether was removed from the extract and the residue distilled under reduced pressure. The yields of 2-phenylethyl chloride for the duplicate runs were 3.72 and 3.86 gm. (65 and 67%, respectively).

Reaction with Hydrobromic Acid

A mixture of 5.00 gm. of 2-phenylethanol-1-C^{14} and 28 gm. of 48% hydrobromic acid was heated under reflux, with occasional shaking, for two hours. After the resulting mixture was cooled to room temperature, it was poured into ice water and extracted with ether. The extract was washed with water and 10% sodium bicarbonate solution and dried over anhydrous sodium sulphate. The ether was evaporated off and the residue distilled under reduced pressure. The yields of 2-phenylethyl bromide, b.p. 110–113°C. at 17 mm. (lit.(7) b.p. 108–112°C. at 17 mm.), for the duplicate runs were 6.30 and 6.05 gm. (83 and 80%, respectively).

Reaction with Hydroiodic Acid

2-Phenylethanol-1-C^{14} (5.00 gm.) and 55% hydroiodic acid (38 gm.) were refluxed for two hours. The resulting mixture was worked up as described in the reaction with hydrobromic acid. The yield of 2-phenylethyl iodide, b.p. 115–118°C. at 14 mm. (lit.(12) b.p. 114–116°C. at 12 mm.), was 8.75 gm. (92%). In a duplicate preparation using 4.00 gm. of the labeled alcohol, the yield of the iodide was 6.88 gm. (90%).

Reaction with Phosphorus and Iodine

To a mixture of 4.00 gm. of 2-phenylethanol-1-C^{14} and 0.35 gm. of red phosphorus in a 100 ml. round-bottomed flask fitted with a reflux condenser was added 4.40 gm. of iodine in small portions with shaking at room temperature. A slight warming up of the reaction mixture resulted. After the addition of iodine had been completed, the mixture was heated over a steam bath for one hour. After the mixture was cooled, ether was introduced to dissolve the product. The ether solution was filtered through glass wool, washed with dilute sodium hydroxide solution and distilled water, dried over anhydrous sodium sul-

phate, and evaporated over a steam bath to give a residue which on fractionation under reduced pressure gave 2-phenylethyl iodide, b.p. 115–118°C. at 14 mm. The yields for duplicate runs were 6.14 and 6.46 gm. (81 and 85%, respectively).

Hydrocinnamic Acid from 2-Phenylethyl Halides

The phenylethylmagnesium halide was prepared in the conventional way and treated with excess solid carbon dioxide. The resulting reaction mixture was acidified and extracted with ether. After the solvent was evaporated off from the ethereal extract, the residue was taken up in dilute sodium hydroxide solution and washed with ether to remove any unreacted organic halide. The product was then precipitated by acidifying the washed sodium hydroxide solution and again recovered by extraction with ether. After the extract was dried over anhydrous sodium sulphate, the ether was removed from this final extract and the residue was crystallized from petroleum ether (b.p. 40–60°C.). Colorless needles of hydrocinnamic acid were obtained which melted alone, or on admixture with an authentic sample, at 48–49°C. (lit.(3) m.p. 48.6°C.). The yields based on the various samples of 2-phenylethyl halides used ranged from 70 to 80%.

Oxidation to Benzoic Acid

2-Phenylethanol-1-C^{14} or hydrocinnamic acid was oxidized to benzoic acid with potassium permanganate in sodium hydroxide solution according to a method previously described (5). The yields obtained generally exceeded 80%.

The oxidation of 2-phenylethyl iodide to benzoic acid was effected as follows. Three grams of 2-phenylethyl iodide was heated under reflux until it was nearly boiling. A saturated aqueous solution of potassium permanganate was added gradually whereby a very vigorous reaction took place. After a total of about 10 gm. of potassium permanganate, as a saturated solution, was added, the reaction mixture was allowed to reflux for one half hour. The product was worked up as previously described (5). It was further purified by dissolution in sodium hydroxide and washed with ether as indicated in the preparation of hydrocinnamic acid. The final yield of benzoic acid, crystallized from water, was 0.54 gm. (34%).

ACKNOWLEDGMENT

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AMINO ACIDS

I. PREPARATION AND PROPERTIES OF GLYCOCYAMIDINE[1]

By A. F. McKay,[2] R. O. Braun, and W. G. Hatton

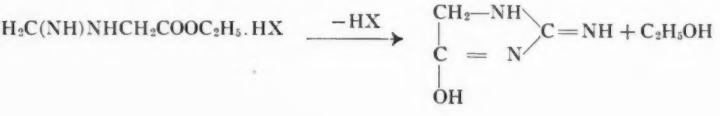
ABSTRACT

Attempts to prepare glycocyamidine by the cyclization of ethyl guanidoacetate in aqueous solutions gave mixtures of guanidoacetic acid and glycocyamidine. The properties of a sample of pure glycocyamidine, which was obtained from the reaction of guanidine with ethyl glycinate, are described.

Glycocyamidine hydrochloride (5) and glycocyamidine sulphate (1) have been prepared in good yields by heating guanidoacetic acid in concentrated hydrochloric acid solution and in normal sulphuric acid solution respectively. However no good methods are available for the preparation of the free base glycocyamidine. Several methods of preparing free glycocyamidine were investigated and the authors found that glycocyamidine could be obtained free from guanidoacetic acid only when the glycocyamidine was prepared under anhydrous conditions.

Glycocyamidine was obtained in 39% yield by treatment of guanidine with ethyl glycinate in absolute alcohol. The other product of this reaction was an oil which gave a picrate melting at 336.5°C. with decomposition. This oil appeared to be a polymer and it has not been further identified. The glycocyamidine prepared in this manner was shown to be free from guanidoacetic acid by paper chromatography. A sample of this glycocyamidine in a nitration medium of nitric acid – acetic anhydride gave glycocyamidine nitrate.

An attempt to prepare glycocyamidine by heating a mixture of guanidine carbonate and glycine gave guanidoacetic acid in agreement with the observations of Nencki and Sieber (7). Finally several experiments designed to prepare glycocyamidine (II) by the removal of acid from ethyl guanidoacetate salts (I) in aqueous solutions always gave a mixture of guanidoacetic acid (glycocyamine) and glycocyamidine. Hydrochloric acid was removed from an aqueous solution of ethyl guanidoacetate hydrochloride by passage of this solution through a bed of IRA-400 resin. On concentration of the aqueous eluate first guanidoacetic acid and then a mixture of guanidoacetic acid and glycocyamidine were obtained. These two crops of crystals were examined by



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[2]*Monsanto Canada Ltd., Ville La Salle, Quebec.*

paper chromatography. A similar result was obtained when an aqueous solution of the picrate of ethyl guanidoacetate was passed through a column of IRA-400 resin.

EXPERIMENTAL[3]

Ethyl Glycinate

Ethyl glycinate (b.p.$_{18}$ 59.5–61°) was prepared in 96.1% yield by the method of Viscontini (9).

Glycocyamidine

Guanidine carbonate (10 gm.) was converted into free guanidine by the method of Morrell and Bellars (6). This guanidine solution was evaporated at 20–25° *in vacuo* (15 mm.) to remove the water. The residual oil was dissolved in 50 cc. of absolute ethanol and the remaining insoluble guanidine carbonate removed by filtration. The filtrate was made up to 100 cc. in a volumetric flask and a 2 cc. aliquot was used for guanidine estimation by precipitation as guanidine picrate. This procedure gave ethanolic solutions containing 4.07–4.42 gm. (62.7–68%) of free guanidine.

When an ethanolic solution of free guanidine was added to an ethanolic solution of ethyl glycinate according to the procedure of Traube and Asher (8), a 24–29% yield of glycocyamidine was obtained. The remaining product was an oil which gave a picrate melting at 336.5°C. Anal. Calc. for $(C_{12}H_{13}N_{10}O_{11})_n$: C, 30.45; H, 2.74; N, 29.58. Found: C, 30.24; H, 2.84; N, 29.68.

The yield of glycocyamidine was increased slightly by the following modification in procedure. Absolute ethanol (50 cc.) was placed in a 500 cc. RB-5-necked flask fitted with two addition funnels, a stirrer, a condenser, and a nitrogen lead-in. An ethanolic solution of guanidine (4.0 gm., 0.068 mole of guanidine in 98 cc. of absolute ethanol) and a solution of ethyl glycinate (7.5 gm., 0.072 mole of ethyl glycinate in 100 cc. of absolute ethanol) were added simultaneously over a period of one hour to the refluxing ethanol. This reaction was carried out under an atmosphere of nitrogen. After removal of the ethanol at reduced pressure, a semisolid remained, yield 8.73 gm. This material was triturated with 10 cc. of ethanol and then it was filtered. The insoluble material did not melt up to 300° and it gave a picrate melting at 208–209°C. Two crystallizations from water raised the melting point to 214–215°C. This picrate was identified as glycocyamidine picrate by mixed melting point determination with an authentic sample. The yield of glycocyamidine was 2.35 gm. (35%). The ethanol filtrate from the glycocyamidine on removal of the ethanol by evaporation gave 5.98 gm. of viscous oil. This oil gave the picrate described above as melting at 336.5°C.

Guanidoacetic Acid

Method A

A mixture of 25 gm. (0.277 mole) of guanidine carbonate, 20.6 gm. (0.275 mole) of glycine, and 1 gm. of ammonium chloride were mixed in a porcelain

[3] *All melting points are uncorrected. The microanalyses were carried out by Micro-Tech Laboratories, Skokie, Ill.*

evaporating dish. This mixture was heated at 100–160°C. with stirring for one hour and 40 min. During this time there was a strong evolution of ammonia. The cooled solid was triturated with water (127 cc.) and filtered to give 15.8 gm. (55.5%) of insoluble material which did not melt up to 300°C. This material was crystallized twice from water (23 cc./gm.) for analysis. Calc. for $C_3H_7N_3O_2$: C, 30.79; H, 5.99; N, 35.90. Found: C, 31.15; H, 5.80; N, 35.80.

An aliquot (27 cc.) of the original filtrate was treated with a saturated aqueous picric acid solution. This gave 1.5 gm. of a picrate (m.p. > 350°C.) which was identified as guanidine picrate by analysis. Thus 8.8% of the original guanidine carbonate remained unchanged. There was no evidence of the presence of glycocyamidine in the filtrate from the guanidoacetic acid. Calc. for $C_7H_8N_6O_7$: C, 29.18; H, 2.77; N, 29.18. Found: C, 29.58; H, 2.78; N, 29.62.

Method B

Guanidoacetic acid was prepared also from glycine and methyl isothiourea sulphate in 81% yield by the method of Brand and Brand (3).

Ethyl Guanidoacetate Hydrochloride

Guanidoacetic acid (36.0 gm., 0.308 mole) was dissolved in 200 cc. of absolute ethanol containing 34 gm. (0.924 mole) of anhydrous hydrogen chloride by refluxing for two hours. Then 100 cc. of the ethanol was removed by distillation and 210 cc. of benzene was added. This solution was distilled using a 12 in. Vigreux column to remove the benzene–ethanol–water and benzene – ethanol azeotropes. Finally the remaining ethanol solution was concentrated *in vacuo* to remove the last traces of ethanol. A heavy viscous sirup was obtained, yield 55.4 gm. (99.3%). A small sample of this product was converted to the picrate in the usual manner. It melted at 189.5–190.5°C., yield 85%. Anal. Calc. for $C_{11}H_{14}N_6O_9$: C, 35.30; H, 3.77; N, 22.45. Found: C, 35.30; H, 3.97; N, 22.27.

Preparation of Glycocyamidine from Ethyl Guanidoacetate

Method A

A 7% aqueous solution of ethyl guanidoacetate hydrochloride (71.8 gm., 0.395 mole) was passed through a bed of IRA-400 resin (885 ml. of IRA-400 resin with a cross sectional area of 28.5 cm.^{2}) at a rate of 25 cc. per minute. Then the column was washed. The total volume of effluent and washings was 16 liters. After removal of the water under vacuum, a total of 35.3 gm. of solid was obtained. The first crop (17.6 gm.) was shown by paper chromatography to be pure guanidoacetic acid while the second crop (17.7 gm.) was found to consist of a mixture of glycocyamidine and guanidoacetic acid. A sample of the second crop was converted to a picrate in the usual manner, yield 79.3%. Two crystallizations from water raised the melting point to 214.5–215.5°C. Anal. Calc. for $C_9H_7N_6O_8$: C, 32.93; H, 2.45; N, 25.62. Found: C, 32.94; H, 2.81; N, 25.25.

Method B

Ethyl guanidoacetate picrate (6.80 gm., 0.018 mole) was dissolved in 2500 cc. of cold water and then passed through a 50 cc. bed of IRA-400 resin (cross sectional area, 2.27 cm.^{2}). The resin column was then washed with a further 1000 cc. of water. The effluent and washings were combined and concentrated to a volume of 25 cc. *in vacuo*. This solution was then poured into 10 volumes of acetone and the precipitate removed by filtration, yield 1.01 gm. (55.5%). This product was identified as glycocyamidine by a comparison of its infrared spectrum with that of an authentic sample of glycocyamidine. On treatment with a saturated aqueous solution of picric acid, it gave glycocyamidine picrate (m.p. 213–215°C.). Found: C, 32.78; H, 2.66; N, 25.72%.

Glycocyamidine Nitrate

The nitrating medium was prepared by adding 8.4 cc. (0.2 mole) of absolute nitric acid (sp. gr. 1.5) to 20 cc. of acetic anhydride in the cold (0°C.). To this solution, 2 gm. (0.02 mole) of glycocyamidine was added and the mixture held at 0–12°C. for one hour and 30 min. This mixture was poured onto 200 gm. of crushed ice and the aqueous solution, after the ice had melted, was extracted with ether (2 × 100 cc.). The aqueous fraction was evaporated *in vacuo* and the residue treated with 25 cc. of absolute alcohol. Then the alcohol was removed *in vacuo* and the residue again treated with 25 cc. of absolute alcohol. After the alcohol was removed once more *in vacuo*, a white solid (m.p. 133°C. dec.) was obtained, yield 0.785 gm. (24%). Two crystallizations from absolute ethanol (25.5 cc./gm.) raised the melting point to a constant value of 145°C. with dec., yield 0.52 gm. Anal. Calc. for $C_3H_6N_4O_4$: C, 22.22; H, 3.70; N, 34.56%. Found: C, 22.33; H, 3.69; N, 34.55%.

This compound gave a positive test for the nitrate ion with Nitron reagent (4).

Paper Chromatography

In all cases 0.013 cc. of the 2% solutions were spotted at the zero point on No. 4 Watmann Chromatography paper. The chromatogram was developed with the upper layer of a mixture of 250 cc. of *n*-butanol, 250 cc. of water, and 60 cc. of glacial acetic acid and the chromatogram was sprayed with the Sakaguchi reagents as outlined by Block, LeStrange, and Zweig (2). In Fig. 1, columns I and II represent chromatograms of pure guanidoacetic acid and glycocyamidine respectively. Columns III and IV are chromatograms of samples from the first and second crops obtained from the eluate from passing ethyl guanidoacetate hydrochloride through a bed of IRA-400 resin. The first crop appears as pure guanidoacetic acid while the second crop is shown to be a mixture of glycocyamidine and guanidoacetic acid. Finally Column V is a chromatogram of the solid obtained from the eluate from the passage of ethyl guanidoacetate picrate through a bed of IRA-400 resin. The R_f values for pure guanidoacetic acid and glycocyamidine were 0.31 and 0.45 respectively when the above solvent mixture was used.

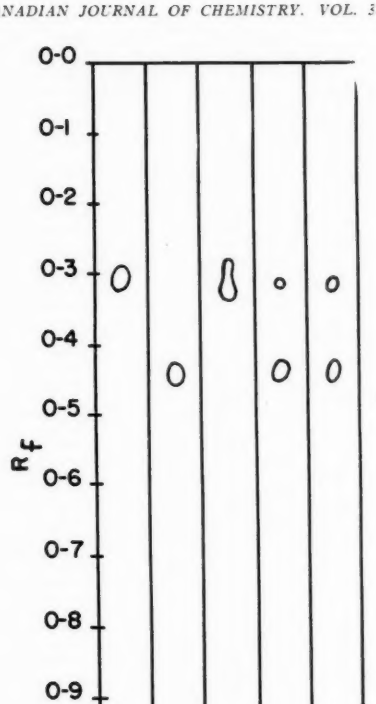

FIG. 1. Chromatograms.

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DETERMINATION OF THE ABSOLUTE FISSION YIELD OF Ba^{140} IN THERMAL NEUTRON FISSION OF U^{235} [1]

By L. Yaffe,[2] H. G. Thode,[3] W. F. Merritt, R. C. Hawkings, F. Brown, and Rosalie M. Bartholomew

ABSTRACT

The absolute fission yield of Ba^{140} in the thermal neutron fission of U^{235} has been determined to be $(6.32 \pm 0.24)\%$. The reaction $B^{10}(n, \alpha)Li^{7}$ was used as a neutron monitor and the B^{10}/B^{11} ratio determined mass spectrometrically before and after neutron bombardment. The Ba^{140} disintegration rate was determined using 4π counting techniques. The half-life of La^{140} has been found to be 40.31 ± 0.06 hr.

INTRODUCTION

Absolute fission yields were first determined by Anderson *et al.* (2). Uranyl sulphate and later manganese sulphate were irradiated in the same position in a neutron beam obtained from a cyclotron. The nuclear reaction $Mn^{55}(n, \gamma)Mn^{56} \xrightarrow{\beta}$ was used as a monitor of the neutron flux. The Ba^{140} was separated radiochemically. The value obtained for the fission yield of Ba^{140} was 8.4%.

Accurate values of the fission and capture cross sections of uranium and manganese respectively and good absolute disintegration rate determination techniques are necessary for this method to yield accurate results. Since no indication is given by Anderson *et al.* of the cross-section values used, their result cannot be recalculated in terms of more recent values for those constants.

To avoid the difficulties due to reproducibility of neutron flux caused by positioning and variations due to the fact that the neutron monitor was irradiated at a time different from the sample itself, Grummitt *et al.* (18) irradiated natural uranium and used the reaction $U^{238}(n, \gamma)U^{239} \xrightarrow{\beta}$ as an internal monitor.

Then

$$N_{U^{239}}/N_{Ba^{140}} = \sigma_c/\sigma_f . Y_f$$

where $N_{U^{239}}$ and $N_{Ba^{140}}$ are the 'steady state' activities of U^{239} and Ba^{140}, σ_c and σ_f are the capture and fission cross sections of natural uranium respectively and Y_f is the fission yield. Again accurate cross-section data and accurate absolute disintegration rate determination methods are essential. The value obtained was 5.6%.

Using more recent values for the capture cross section of U^{238} ($\sigma_c = 2.80 \times 10^{-24}$ cm.^{2} for 2200 meters/sec. neutrons (9)) and for the thermal neutron fission cross section of natural uranium due to U^{235} ($\sigma_f = 3.95 \times 10^{-24}$ cm.^{2} (3, 9)), this result for the absolute fission yield of Ba^{140} becomes 6.0%.

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Contribution from Atomic Energy of Canada Limited, Chalk River, Ontario. Issued as A.E.C.L. No. 133.
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Absolute fission yield experiments are described by Freedman and Steinberg (16) in a paper summarizing work done by themselves and colleagues in the Manhattan Project. The technique used was to irradiate simultaneously in the same neutron flux a thick and a thin piece of uranium. Fissions from the thin sample were counted in a pulse ionization chamber. Radiochemical analyses were performed on the thick piece.

Using the above method, Engelkemeir *et al.* (13) obtained a value of 5.8% for the fission yield of Ba^{140}. They used a value of 12.5 days for the half-life rather than the presently accepted value of 12.8 days (12). Use of the latter value would give a slightly higher yield. Freedman and Engelkemeir (15) using the same equipment, but improved techniques, obtained a value of $6.15 \pm 0.13\%$ for the absolute fission yield of Ba^{140}.

The chief error in this experiment lies in the determination of the absolute disintegration rate of Ba^{140}. Using the best available absorption and scattering data for Ba^{140}, Steinberg (23) corrected the results of Freedman and Engelkemeir yielding a value of 6.17. In a private communication Steinberg (22) has given us a reassessed value of 6.32 ± 0.6 as the best value for this experiment.

In the above experiment several sources of error are possible. First, in the fission counter, where the "geometry" is assumed to be 50%, corrections have to be made for coincidences, pulse height selection, and fission background of the chamber. These corrections can be made to $\pm 2\%$ according to Steinberg. Secondly, one assumes that the fission rate per U atom in the thick and thin samples is identical. Thirdly, the following corrections have to be made to the experimentally determined counting rate of Ba^{140} to transform it into an absolute disintegration rate.

(*a*) Self-scattering and self-absorption.

(*b*) Back-scattering.

(*c*) Absorption in counter window of Geiger counter and air gap between the sample and counter window.

(*d*) Geometrical efficiency of the counter.

All of these corrections, some of which are not negligible, have caused Steinberg to put an error of $\pm 10\%$ on the absolute measurement of Ba^{140}.

We have measured the absolute fission yield of Ba^{140}. Instead of the fission chamber arrangement we have used the change in the ratio of B^{10}/B^{11} before and after irradiation as a neutron flux monitor. One eventually has to turn to a fission chamber determination to obtain a value for the fission cross-section σ_f. However, this can be done very accurately in an experiment designed specifically to obtain this result.

By the use of a 4π type of counter (7, 19) we have avoided the necessity of using the correction factors previously described; thus there resulted better accuracy in the determination of the Ba^{140} disintegration rate.

EXPERIMENTAL

(i) *Irradiation*

A purified sample of boron trifluoride was divided into two parts, each

sealed into a quartz tube at a pressure of about 30 cm. of mercury. One was irradiated with the uranium metal, the other was kept for later reference.

The accurately weighed sample of uranium metal (about 600 mgm.) was placed in a 'self-serve' irradiation container along with the sample of boron trifluoride. The irradiation container was evacuated and the container sealed *in vacuo* using the cold welding technique (1). The uranium metal, after irradiation, showed no signs of oxidation testifying to the efficacy of the cold-weld sealing technique. The sample showed a loss of weight of only 0.0006 gm. after the irradiation period of 36 days in the NRX reactor.

(ii) *Mass Spectrometry*

A conventional 180° direction focusing mass spectrometer with vibrating reed d-c. amplifier and speedomax recorder was used to compare the isotopic ratios of the irradiated and unirradiated part of the boron trifluoride sample.

The ratio of B^{10}/B^{11} before irradiation to that after irradiation for the sample in question was found to be 1.029 ± 0.001. An accuracy of 0.1% is about the best obtainable at the present time when single ion collection methods are used, particularly where fluorides are involved. However, the samples have been retained and isotopic ratios can be redetermined later using the simultaneous collection system of ion measurement. A simultaneous collection instrument used for the rapid comparison of isotopic ratios is now being adapted for use with boron.

(iii) *Chemical Separation*

The uranium metal was dissolved in nitric acid to which 50 mgm. barium nitrate carrier had been added. Barium was separated from the mixture using a method previously described (17). It consisted of chloride, chromate, and nitrate separations with the addition of appropriate holdback carriers. The final barium nitrate precipitate was dissolved in water and made up to a constant volume. From this, small aliquots were taken with calibrated micropipettes for measurement purposes. The chemical yield, determined gravimetrically by the precipitation of barium as barium sulphate from the remainder of the solution, was 72.9%.

(iv) *Counting*

The disintegration rate of $Ba^{140}+La^{140}$ was determined using the 4π counting technique (19). Counting samples were prepared by the evaporation, under an infrared lamp, of known aliquots of the barium nitrate solution on a thin (100 μgm./cm.^{2}) polystyrene film which had a conducting film of gold (25 μgm./cm.^{2}) on each side. Self-absorption in the source material (i.e. barium nitrate) was largely eliminated by the technique of successive dilutions and by taking care to spread the material as uniformly as possible. The small self-absorption loss due to the finite size of the crystals constituting the source cannot be eliminated in this manner but is considered negligible in this case (i.e. $<1\%$).

Corrections were made for absorption of beta particles in the thin plastic film and for coincidence losses in the counting apparatus. The total correction required for the above losses was usually less than two per cent.

Corrections were also made to the counting data for growth and decay in the Ba^{140}–La^{140} system during the time interval between the last separation of Ba^{140} from its daughter La^{140} and the time of counting. This correction is discussed in detail in the following section.

(v) *Growth and Decay Correction*

If one assumed a steady build-up of Ba^{140} the saturation factor for the irradiation period used would have been 85.8%. One must, however, take into account neutron flux variations which occurred during the course of the irradiation. Conditions during this experiment were such that one could, with a maximum error of $\pm 0.5\%$, assume that the reactor power was proportional to the neutron flux. An analogue computer, designed by Bayly (5), was used to establish the "effective" saturation factor as $(58.0 \pm 0.3)\%$. The samples were of such a size that no correction for perturbation of the neutron beam had to be made (21).

The half-life of La^{140} is given by Weimer *et al.* (25) as 40.0 ± 0.3 hr. over 11 half-lives from neutron bombardment of spec-pure lanthanum oxide. Bothe (8) observed a period of 39.5 ± 0.5 hr. with thermal neutrons on La^{139}. Cork *et al.* (10) followed the decay of La^{140} prepared by (n, γ) reaction of pile neutrons on specially purified La^{139} through eight half-lives to get a half-life of 41.4 hr. Ballou *et al.* (4) irradiated two samples of lanthanum nitrate with neutrons from cyclotron deuterons on beryllium. The first sample gave 39.5 hr. over 8 half-lives, and the second 40.3 hr. over about 13 half-lives for an average of 40.0 ± 0.5 hr. Bishop *et al.* (6) observed a half-life of 40.0 ± 0.1 hr. Using the 4π counter, we have followed the decay of a sample of La^{140} produced by thermal neutron bombardment of spectroscopically pure La_2O_3 for 14 half-lives. A least squares analysis of the counting data gave the half-life of La^{140} as 40.31 ± 0.06 hr. This is in excellent agreement with the value of 40.3 hr. obtained by Ballou over a corresponding interval.

Cork *et al.* (11) report a half-life of 13.4 days for Ba^{140}. Engelkemeir *et al.* (12) have followed the decay of Ba^{140} for periods up to about 12 half-lives and obtained a value of 12.8 days. We have used 12.8 days as the half-life for Ba^{140} in all our calculations. This value has been found to give a good fit to our experimental data followed over periods of up to five half-lives of Ba^{140}.

The total disintegration rate of the separated Ba^{140} was found to be $5.395 \pm 0.067 \times 10^8$ dis./sec. corrected to the end of the irradiation. From this must be subtracted a fast fission contribution (21) of $(0.8^{+0.6}_{-0.3})\%$. The loss of Ba^{140} by recoil of the fission fragments from the unwrapped uranium is estimated to be $(0.3^{+0.0}_{-0.1})\%$. The other experimental values pertinent to a calculation of a value for the fission yield of Ba^{140} are tabulated below:

Weight of uranium metal	= 646.5 mgm.
Effective saturation factor	$= (58.0 \pm 0.3)\%$.
Chemical yield (barium separation)	$= (72.9 \pm 0.4)\%$.
Ratio of B^{10}/B^{11} before irradiation to B^{10}/B^{11} after irradiation	$= 1.029 \pm 0.001$.
Actual running time of reactor (t)	$= 2.429 \times 10^6$ sec.

The effective flux of thermal neutrons may be calculated from the experimental data as follows:

[1] $$dN/dt = -N(\rho v)_{th}\sigma_B$$

or,

[2] $$N = N_0 \exp[-(\rho v)_{th}\sigma_B t].$$

N = number of B^{10} atoms present at any time t,
$(\rho v)_{th}$ = effective thermal neutron flux,
σ_B = thermal neutron capture cross section of B^{10},
N_0 = number of B^{10} atoms present when $t = 0$.

The thermal neutron absorption cross section of B^{10} is usually attributed to the reaction $B^{10}(n, \alpha)Li^7$. Since we have used the change in the ratio of B^{10}/B^{11} as a measure of the integrated thermal neutron flux any reaction other than the (n, α) reaction which affects this ratio may constitute a source of error. The reaction $B^{11}(n, \gamma)B^{12}$ will not affect the results since the B^{11} capture cross section is known to be small relative to that of B^{10} $(1 : 10^5)$. On the other hand, no experimental evidence exists as to the cross section for the reaction $B^{10}(n, \gamma)B^{11}$.

For the conditions of this experiment calculations show that a cross section for this reaction of approximately 80 barns would result in an error equal to the limit of the error in the mass spectrometer analysis. A cross section of approximately 20 barns would be completely negligible insofar as this experiment is concerned. We have assumed, therefore, that the cross section for the reaction $B^{10}(n, \gamma)B^{11}$ does not exceed 20 barns so that the change in the ratio of B^{10}/B^{11} as measured mass spectrometrically gives the change in the number of B^{10} atoms as a result of the irradiation and the error given for the mass spectrometric analysis represents the analytical error.

Thus,

[3] $$\frac{N_0}{N_0 \exp[-(\rho v)_{th}\sigma_B t]} = 1.029$$

or,

$$\exp[(\rho v)_{th}\sigma_B t] = 1.029$$

whence

$$(\rho v)_{th}\sigma_B t = 0.0286$$

and

[3a] $$(\rho v)_{th} = 0.0286/\sigma_B t.$$

The rate of depletion of U^{235} may be expressed by

[4] $$dU/dt = -U(\rho v)_{th}\sigma_{abs}$$

or,

[4a] $$U = U_0 \exp[-(\rho v)_{th}\sigma_{abs} t]$$

where

U = number of U^{235} atoms present at time t,
U_0 = number of U^{235} atoms when $t = 0$,
$(\rho v)_{th}$ = effective thermal neutron flux,
σ_{abs} = thermal neutron absorption cross section of U^{235}.

In terms of the U^{235} present initially, the fission rate is therefore

[5] $$[dU/dt]_{fission} = -\{U_0 \exp[-(\rho v)_{th}\sigma_{abs} t]\}(\rho v)_{th}\sigma_f$$

$$= -[U_0(\rho v)_{th}\sigma_f] \exp[-(\rho v)_{th}\sigma_{abs}t]$$

where σ_f = thermal neutron cross section for fission of U^{235}.

We may then write for the net rate of formation of Ba^{140} at any time t during the irradiation,

[6] $$dX/dt = -Y_f[dU/dt]_{fission} - \lambda X$$

where

X = number of atoms of Ba^{140} at any time t,
Y_f = thermal neutron fission yield for Ba^{140},
λ = disintegration constant for Ba^{140}.

From equations [5] and [6] we have

[7] $$dX/dt = Y_f[U_0(\rho v)_{th}\sigma_f] \exp[-(\rho v)_{th}\sigma_{abs}t] - \lambda X.$$

Integrating and multiplying through by λ, equation [7] becomes

[8] $$X\lambda = \frac{\lambda Y_f[U_0(\rho v)_{th}\sigma_f]}{\lambda - (\rho v)_{th}\sigma_{abs}}\{\exp[-(\rho v)_{th}\sigma_{abs}t] - \exp(-\lambda t)\}.$$

Substituting for $(\rho v)_{th}$ from equation [3*a*] we may write for the disintegration rate of Ba^{140}

[9] $$X\lambda = \frac{\lambda Y_f[(0.0286/t)U_0(\sigma_f/\sigma_B)]}{\lambda - (0.0286/t)(\sigma_{abs}/\sigma_B)}[\exp(-0.0286\sigma_{abs}/\sigma_B) - \exp(-\lambda t)].$$

Investigations into the natural abundance of the boron isotopes have been carried out by Inghram (20) who obtained a B^{11}/B^{10} ratio of 4.31 (i.e. 18.83% B^{10}). Thode *et al.* (24) showed that a variation of about four per cent occurred in the natural abundance depending on the geographical location from which the boron had been obtained. However the actual boron samples used gave an abundance ratio identical with that found by Inghram for American borax.

Thus,

$$\sigma_{abs}/\sigma_B = 0.90 \times 0.1883 = 0.169$$

where 0.90 has been taken as the value for the ratio of the absorption cross section of U^{235} (σ_{abs}) to the capture cross section of natural boron, under the conditions of the experiment (i.e. a Maxwellian distribution of neutrons at 57°C).

Evaluating the terms of equation [9] which involve σ_{abs}/σ_B we find

$$\lambda - (0.0286/t)(\sigma_{abs}/\sigma_B) = 6.27 \times 10^{-7} - 1.99 \times 10^{-9} = 6.25 \times 10^{-7}$$

and

$$\exp(-0.0286\ \sigma_{abs}/\sigma_B) = 0.995.$$

It is obvious that even a large change in the value of σ_{abs}/σ_B will not appreciably affect the final result.

The ratio σ_f/σ_B is a quantity which is usually determined experimentally. Since the ultimate value of Y_f is critically dependent on this ratio it was thought desirable to use it as a standard rather than the independent values of the two constants. Thus the value for Y_f may be easily adjusted in accordance with any subsequent revisions in the value of the ratio σ_f/σ_B.

We have used a ratio of 0.773 for σ_f/σ_B for natural boron having an isotopic composition identical with that used in our experiment. The ratio already takes into account the fact that our irradiation occurred in a beam of neutrons having a Maxwellian distribution corresponding to a temperature of 57°C.

For B^{10}

$$\sigma_f/\sigma_B = 0.1883 \times 0.773 = 0.1456.$$

From equation [9]

$$Y_f = \frac{X\lambda[\lambda - (0.0286/t)(\sigma_{abs}/\sigma_B)]}{\lambda[(0.0286/t)\cdot U_0(\sigma_f/\sigma_B)]\{\exp(-0.0286\,\sigma_{abs}/\sigma_B) - \exp(-\lambda t)\}}.$$

Evaluating the remaining factors in the above equation we find the value for

$$X\lambda = \frac{5.395 \times 10^8 \times 0.992}{0.729 \times 0.997} = 7.363 \times 10^8 \text{ dis./sec.}$$

where 0.992 is the correction factor to bring the result to that resulting from thermal neutron fission alone, 0.729 is the correction for chemical recovery, and 0.997 is the correction for recoil loss.

$$\lambda = \frac{0.6932}{12.8 \times 3600 \times 24} = 6.27 \times 10^{-7}\text{sec.}^{-1},$$
$$t = 2.429 \times 10^6\text{sec.},$$

and

$$U_0 = \frac{0.6465 \times 6.025 \times 10^{23} \times 0.00719}{238.07} = 1.176 \times 10^{19} \text{ atoms}$$

where 0.00719 is the value for the natural abundance of U^{235}(14) and $\exp(-\lambda t)$ $= 1 -$ effective saturation factor $= 1 - 0.580 = 0.420$. Therefore,

$$Y_f = \frac{7.363 \times 10^8}{6.27 \times 10^{-7}} \cdot \frac{6.27 \times 10^{-7} - 2.01 \times 10^{-9}}{1.178 \times 10^{19} \cdot 1.177 \times 10^{-8} \cdot (\sigma_f/\sigma_B)} \cdot \frac{1}{0.995 - 0.420}$$
$$= \frac{9.206 \times 10^{-3}}{\sigma_f/\sigma_B}$$
$$Y_f = \frac{9.206 \times 10^{-3}}{0.1456} = 6.32\%.$$

The errors involved in our measurement are:

(*a*) disintegration rate (standard)	1.2%
(*b*) mass spectrometer analysis (average deviation)	3.4%
(*c*) chemical yield (average deviation of three results)	0.5%
(*d*) fast fission contribution (estimated maximum)	0.6%
(*e*) saturation factor (estimated maximum)	0.5%
(*f*) fission recoil loss (estimated maximum)	0.1%.

Errors not associated with the measurement but which occur in the calculation are:

(*g*) abundance of U^{235} in natural uranium,
(*h*) abundance of the boron isotopes,
(*i*) the ratio σ_f/σ_B.

The errors in (*g*) and (*h*) are small. No error is included for the value of σ_f/σ_B chosen. Should a better value be available our result need be corrected only by the ratio of the new value to the old.

Treating the errors listed ((*a*)–(*f*)) as standard errors the thermal neutron fission yield of Ba^{140} is $(6.32 \pm 0.24)\%$.

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THE POLAROGRAPHIC REDUCTION OF AMARANTH[1]

By G. G. McKeown and J. L. Thomson

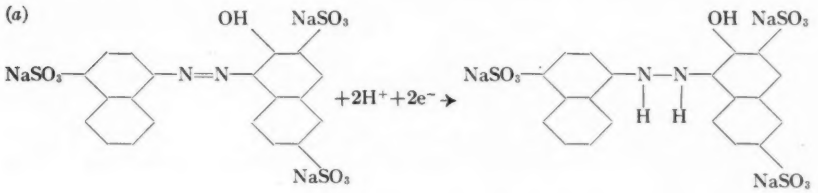
ABSTRACT

Amaranth, a food color, has been studied polarographically over a pH range of 2.0 to 10.0 in aqueous solution and was found to give a well-defined wave, diffusion controlled and suitable for quantitative work. Irreversibility was indicated by the behavior of the half-wave potential to changes in pH and concentration. With pH, a direct relationship of −0.080 v. per pH unit held between pH 2.0 and 7.0, while with concentration, the half-wave potential was found to apparently vary directly with the logarithm of concentration. Using a coefficient of diffusion value obtained by conductance measurements the value of n for the reaction was calculated to be 4, which corresponds to a rupture of the azo group to yield the corresponding amines.

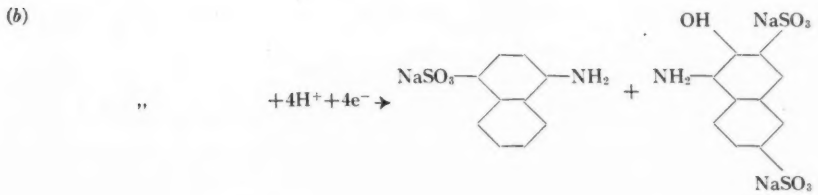
In connection with the work of this laboratory, a study of the polarographic behavior of the artificial food colors was begun with the object of determining the possible value for qualitative and quantitative analysis. This paper is the first of a series and describes the reduction of amaranth at the dropping mercury electrode.

A consideration of the formula of amaranth reveals that two likely possibilities for reduction exist: (*a*) the azo group accepts two hydrogen atoms to form an hydrazo group, and (*b*) the azo group accepts four hydrogen atoms to yield the corresponding amines.

(*a*)



(*b*)



Polarographic work on several compounds similar to amaranth suggests that the former reaction should take place. The azo–hydrazo reaction has been shown to occur with azobenzene and its derivatives (5, 6), although some doubt still exists as to the reversibility of the reaction (7). The azo dyes, orange II and metanil yellow, are claimed to follow a two electron reduction

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Contribution from the Food and Drug Laboratory, Department of National Health and Welfare, Ottawa, Ont.

on the basis of an n value calculated from the wave slope (2). However, this claim would seem to be somewhat doubtful as the wave included an unsuppressed maximum and the behavior of the half-wave potential with changes in pH and concentration indicated the reaction to be irreversible.

On the other hand, amaranth has long been known to undergo a four electron reduction under the influence of chemical reducing reagents. The reaction forms the basis of the quantitative determination of amaranth and similar azo colors by titanium trichloride reduction (4).

EXPERIMENTAL

All current–voltage curves were obtained on a Leeds and Northrup Type E recording polarograph using a polarizing range of 0.0 to −1.0 v., a current range of 20 μa. and damped at position 1 on the instrument. Half-wave potentials were obtained by first determining the diffusion current then manually adjusting the polarizing voltage to give the half value. The characteristics of the capillary of the dropping mercury electrode as determined at a potential of −0.5 v. and a mercury head of 60.0 cm. were m = 1.90 mgm./sec., t = 3.66 sec., and $m^{2/3}\,t^{1/6}$ = 1.90 mgm.$^{2/3}$ sec$^{-1/2}$.

The usual H-type cell was employed containing a saturated calomel electrode as reference anode separated from the electrolysis compartment by a sintered glass disk and an agar plug. The cell was equipped with inlets to admit gas for the deoxygenation of test solutions. All experiments were carried out with the temperature of the cell controlled at 25.0°C.

A commercial sample of amaranth, manufactured by H. Kohnstamm and Co., Inc., New York, was purified by repeated recrystallization from aqueous solutions of sodium acetate. The product was washed with boiling ethanol and dried *in vacuo*. A stock solution of the purified dye in water was prepared and standardized by titanium trichloride titration.

Solutions of the Universal Buffer Mixture of Prideaux and Ward (1) were prepared from reagent grade chemicals for pH values from 2.0 to 10.0. These were checked on a Beckman Model G pH meter.

Gelatin supplied by the British Drug Houses (Canada) was used to suppress maxima.

Tank nitrogen, purified by passage through an acid solution of chromous sulphate, was used to deoxygenate all solutions.

Amaranth was polarographed in aqueous solutions that contained by volume 80% buffer solution and were 0.5 M in potassium chloride as supporting electrolyte. Gelatin, when used to suppress maxima, was present in the amount of 0.01%.

Conductivity measurements were made using a Leeds and Northrup medium conductivity cell equipped with platinum black coated electrodes. All measurements were carried out with the temperature of the cell controlled at 25.0°C.

RESULTS

Preliminary experiments showed amaranth to give a well-defined wave over a wide pH range provided that the solutions were well buffered and contained

a liberal concentration of supporting electrolyte. A maximum appeared on the wave which was readily suppressed by gelatin.

Influence of pH

Polarograms were run of 0.5 mM amaranth buffered at pH values from 2.0 to 10.0. These were done in duplicate, with and without gelatin, to note its effect on the wave. Some typical curves are shown in Fig. 1. Half-wave potentials and diffusion currents are listed in Table I.

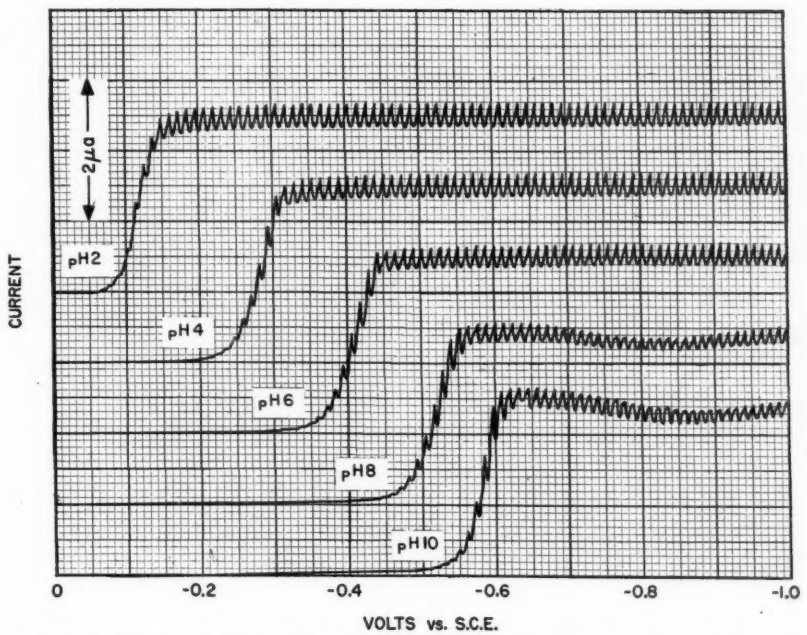

FIG. 1. Current–voltage curves of 0.5 mM amaranth at various pH's. Solutions contained 0.01% gelatin.

TABLE I

HALF-WAVE POTENTIALS (VS. S.C.E.) AND DIFFUSION CURRENTS OF 0.5 mM AMARANTH AT VARIOUS pH VALUES

pH	$-E_{\frac{1}{2}}$ (v.)		i_d (μa.)	
2.0	.118	.110*	5.0	4.9*
3.0	.207	.203*	5.0	4.9*
4.0	.281	.275*	5.0	4.9*
5.0	.368	.348*	5.0	4.9*
6.0	.443	.405*	5.0	4.9*
7.0	.521	.462*	5.0	4.9*
8.0	.579	.516*	5.0	4.9*
9.0	.611	.549*	5.0	4.9*
10.0	.647	.579*	5.0	4.9*

**Solutions were 0.01% in gelatin.*

The maximum appearing in the polarograms of unsuppressed solutions was not sufficiently pronounced to interfere with the measurement of half-wave potentials and diffusion currents. The addition of gelatin, on the other hand, besides suppressing the maximum, caused a slight decrease in the height of the wave and tended to shift the half-wave potential to more positive values, the effect being very noticeable at high pH values.

The half-wave potential was found to vary with the pH in a manner suggesting an irreversible, organic reaction. Between pH 2.0 and 7.0, the relationship was linear with a shift of −0.080 v. per pH unit. Beyond pH 7.0, however, the variation with pH was found to steadily diminish. The results are illustrated in Fig. 2.

The height of the wave was found to be independent of pH.

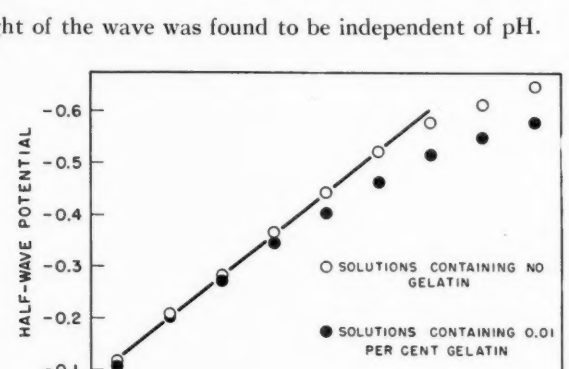

FIG. 2. Effect of pH on the half-wave potential of 0.5 m*M* amaranth.

Influence of Concentration

Polarograms were run of solutions containing amaranth in concentrations ranging from 0.05 to 1.00 m*M*. These were done in duplicate, with and without

TABLE II
HALF-WAVE POTENTIALS (VS. S.C.E.) AND DIFFUSION CURRENTS OF AMARANTH IN VARIOUS CONCENTRATIONS

Concentration (mM.)	$-E_{\frac{1}{2}}$ (v.)						i_d (μa.)					
	pH 4.0		pH 6.0		pH 8.0		pH 4.0		pH 6.0		pH 8.0	
1.00	.311	.302*	.475	.432*	.612	.541*	9.6	9.5*	9.6	9.6*	9.6	9.5*
0.75	.302	.291*	.462	.421*	.602	.531*	7.2	7.2*	7.2	7.1*	7.3	7.2*
0.50	.289	.278*	.444	.406*	.583	.519*	5.0	5.0*	5.0	4.9*	5.0	5.0*
0.25	.270	.260*	.418	.385*	.551	.498*	2.6	2.6*	2.6	2.6*	2.6	2.5*
0.10	.234	.231*	.372	.361*	.505	.477*	1.2	1.2*	1.2	1.2*	1.2	1.2*
0.05	.214	.215*	.346	.342*	.475	.460*	0.6	0.6*	0.6	0.6*	0.6	0.6*

**Solutions were 0.01% in gelatin.*

gelatin, at pH values of 4.0, 6.0, and 8.0. Some typical curves are shown in Fig. 3. Half-wave potentials and diffusion currents are listed in Table II.

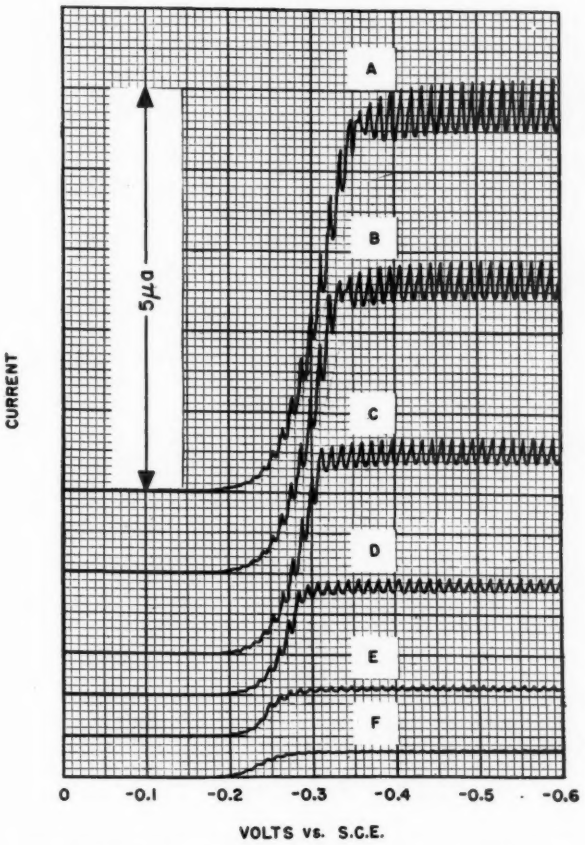

FIG. 3. Current–voltage curves of amaranth in various concentrations—*A*, *B*, *C*, *D*, *E*, and *F* were 1.00, 0.75, 0.50, 0.25, 0.10, and 0.05 m*M* respectively. All solutions contained 0.01% gelatin and were buffered at pH 4.

These results also indicate the reaction to be irreversible. The half-wave potential was found not to remain constant but to shift to more negative values with increasing concentration. This behavior occurred at all three pH values and, as illustrated in Fig. 4, a direct relationship appears to exist between the logarithm of concentration and the half-wave potential for the unsuppressed solutions. In the presence of gelatin, the half-wave potential also varies with concentration but in a non-linear manner. The effect of gelatin becomes almost negligible at low concentrations.

The height of the wave was found to vary directly with the concentration.

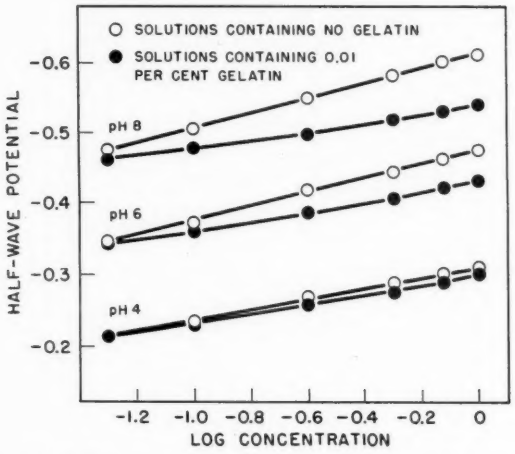

FIG. 4. Effect of concentration on the half-wave potential of amaranth.

Effect of the Mercury Pressure on the Height of the Wave

Wave heights were determined on a 0.5 m*M* amaranth solution at various pressures on the dropping mercury electrode. The results are shown in Table III.

TABLE III
EFFECT OF MERCURY PRESSURE ON WAVE HEIGHT

Pressure (cm. Hg)	Droptime (sec.)	Pressure (corrected)	Current(i) (μa.)	$i/p^{\frac{1}{2}}$
60	3.66	58.4	5.01	.655
55	4.01	53.4	4.78	.654
50	4.48	48.5	4.55	.654
45	5.08	43.5	4.31	.653
40	5.67	38.6	4.06	.653
35	6.49	33.7	3.80	.655
30	7.55	28.7	3.50	.653

It will be seen that the height of the wave is proportional to the square root of the mercury pressure which thus proves the reaction to be diffusion controlled.

Determination of the Diffusion Coefficient of the Amaranthate Ion

In order to calculate the number of electrons involved in a polarographic reaction, the coefficient of diffusion of the ion or molecule being reduced must be known. In this case, amaranth being the trisodium salt of an organic ion, one is concerned with the diffusion coefficient of that ion. While it is difficult to determine the coefficient of diffusion of an ion under the exact experimental conditions of a polarographic reaction, a value at infinite dilution can be readily obtained from conductivity measurements. With low electron numbers,

such values are always sufficiently close to the true values to give the correct solutions.

Electrical conductivities of pure amaranth were determined at 25.0°C. for concentrations ranging from 0.005 to 0.00025 equivalents. By extrapolation, the equivalent conductance at infinite dilution was obtained:

$$\Lambda_{0\text{Am}} = 127.5 \text{ ohms}^{-1} \text{ cm.}^2$$

Applying the equation

$$\Lambda_0 = \lambda^+ + \lambda^-,$$

where the equivalent conductance is equal to the sum of the ionic conductances, and substituting the known value for the sodium ion

$$\lambda^+_{0\text{Na}+} = 50.1 \text{ ohms}^{-1} \text{ cm.}^2$$

the equivalent ionic conductance of the amaranthate ion is obtained:

$$\lambda^-_{0\,\frac{1}{3}\text{Am}---} = 77.4 \text{ ohms}^{-1} \text{ cm}^2.$$

Substituting this value into the equation

$$D_0 = 2.67 \times 10^{-7} \lambda_0 / Z \text{ cm.}^2 \text{ sec.}^{-1} \text{ (Ref. 3)}$$

where the ionic charge Z is equal to 3, the coefficient of diffusion of the amaranthate ion is obtained:

$$D_{0\text{Am}---} = 6.9 \times 10^{-6} \text{ cm.}^2 \text{ sec}^{-1}.$$

CONCLUSIONS

The wave given by amaranth has been shown to be diffusion controlled since its height is proportional to concentration, independent of pH, and varies with the square root of the mercury pressure on the dropping electrode. As the wave is well-defined, producible over a wide pH range, and free from excessive distortion by maxima, it is well suited for quantitative work. The dye may be readily detected in concentration as low as 5 mgm./liter (8.3 μM.) which gives a current of approximately 0.1 μa.

The behavior of the half-wave potential has indicated the reaction to be irreversible. While the half-wave potential is dependent upon the pH as one would expect for an organic reaction, the shift per pH unit exceeds the theoretical values predicted for reversible reactions. In addition, the half-wave potential is not independent of concentration, but apparently varies with its logarithmic value. Provided that proper attention is given to the factors of pH, concentration, the effect of gelatin, etc. on the half-wave potential, the wave could be of value for qualitative identification.

To determine the number of electrons involved in the reaction, the figures from above, $i_d = 1.2$, $C = 0.1$, $D = 6.9 \times 10^{-6}$, and $m^{2/3}\, t^{1/6} = 1.90$, are substituted into the Ilković equation

$$i_d = 607\, n\, CD^{1/2}\, m^{2/3}\, t^{1/6}$$

to give

$$n = 4.0.$$

A transfer of four electrons is in agreement with the second equation as presented above in which the azo group is completely reduced to yield the corresponding amines. This conclusion is substantiated by the fact that the process was found to be irreversible as such a reaction would certainly be.

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n-EICOSENOIC ACID IN SOME NATURAL GLYCERIDE OILS[1]

By C. Y. Hopkins and Mary J. Chisholm

ABSTRACT

n-Eicosenoic acid (as acid or ester) was isolated from the following oils: rutabaga seed (*Brassica napobrassica* Mill.), frenchweed seed (*Thlaspi arvense* L.), dogfish liver (*Squalus acanthias* L.), and the blubber oil of the beluga or white whale (*Delphinapterus leucas* [Pallas]).

The eicosenoic acid from each of these materials was found to have the unsaturation in the 11,12 position. The content of eicosenoic acid in the four oils is estimated as follows (% of the total fatty acids): rutabaga 6, frenchweed 7, dogfish liver 11, beluga 4. The best sources, in respect to yield and purity, were frenchweed seed and rutabaga seed.

The frenchweed oil had the following fatty acid composition (% total fatty acid): saturated acids 3, oleic 16, linoleic 25, linolenic 12, eicosenoic 7, erucic 37.

9-Hexadecenoic acid was identified as a constituent of dogfish liver oil and beluga oil.

INTRODUCTION

n-Eicosenoic acid is available from the seed wax of jojoba (*Simmondsia californica* Nuttall) but the wax alcohols interfere to some extent with the isolation of the acid. Neither the seed nor the wax is offered through ordinary commercial channels. Accordingly an effort has been made to find a glyceride oil having a relatively large content of eicosenoic acid, so as to provide a more convenient source.

The materials chosen for the present work were (*a*) two members of the Cruciferae family, rutabaga and frenchweed, and (*b*) two examples of marine fauna, dogfish and beluga. Certain Cruciferae seed oils have already been shown to contain appreciable amounts of eicosenoic acid (1, 4, 7). The oils of most fish livers and marine mammals have a good proportion of C_{20} acids, although mainly polyenoic. Their value as a practical source of eicosenoic acid has not been determined hitherto.

EXPERIMENTAL

A. Rutabaga Seed Oil

Rutabaga seed (*Brassica napobrassica* Mill.) was supplied by the Canadian Department of Agriculture under the common name "Acadia Swede Seed". The oil content was 31%. It had iodine value 106.7, saponification value 178.4, and unsaponifiable matter 1.8%. The methyl esters were prepared by methanolysis and distilled at a pressure of 0.1 mm. or less in two lots, totalling 595 gm.

Distillation data for one lot are given in Table I.

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TABLE I
DISTILLATION OF METHYL ESTERS OF RUTABAGA SEED OIL

Fraction	Vapor temp., °C. (approx.)	Wt. of fraction (gm.)	Iodine value
1	–115	14.8	68.7
2	115–117	23.5	127.9
3	117–120	35.8	145.1
4	120–123	39.5	141.1
5	123–130	30.4	137.8
6	130–141	8.6	102.9
7	141–145	10.0	82.4
8	145–148	3.5	82.7
9	148–151	17.8	81.3
10	151–162	28.0	75.3
11	162–165	32.0	73.0
R	Residue	43.5	
		287.4	

Fraction 9, judged to be mainly esters of C_{20} acids, was crystallized from acetone and gave the following fractions:

Fraction	Temp. of cryst'n, °C.	Yield, gm.	Iodine value
91	−25	1.4	(Solid)
92	−32	9.2	77.5
93	−50	4.6	79.6
94	Filtrate	2.3	120.9

Fraction 92 was hydroxylated by alkaline permanganate and gave dihydroxyeicosanoic acid readily, m.p. 129–130°, equivalent weight 344.6 (theory 344.5). Fraction 93 was saponified and gave eicosenoic acid, melting after one crystallization at 21° (accepted m.p. 23–24°).

The dihydroxyeicosanoic acid from fraction 92 was subjected to oxidative cleavage by periodate and gave nonaldehyde (semicarbazone, m.p. 99–100°) and 10-aldehydodecanoic acid (semicarbazone, m.p. 159–160°). These products were identified by mixed melting points with authentic specimens. The original acid is therefore *n*-11-eicosenoic acid.

The content of eicosenoic acid is estimated to be about six per cent of the total fatty acids of the oil. Acids higher than C_{20} make up about 35% of the total and the remainder is chiefly C_{18} acids.

B. Frenchweed Seed Oil

Seed of frenchweed (*Thlaspi arvense* L.), also called penny cress, stinkweed, and fanweed, was separated mechanically from the screenings from wheat grown in Western Canada.* The oil, obtained by solvent extraction, had I.V. 119.7, sap. value 176, and unsaponifiable matter 1.7%. Distillation of the methyl esters was carried out at about 0.1 mm. pressure, (Table II).

**Kindly furnished by Alberta Seed Growers' Co-operative Ltd.*

TABLE II
DISTILLATION OF METHYL ESTERS OF FRENCHWEED SEED OIL

Fraction	Vapor temp., °C. (approx.)	Wt. of fraction (gm.)	Iodine value
1	100–132	82.7	153
2	132–136	39.7	165
3	136–147	7.6	108
4	147–153	23.0	94.1
5	153–162	12.6	81.8
6	162–165	68.4	73.5
R	Residue	40.0	
		274.0	

Fraction 4 was crystallized from acetone, taking fractions at −30° and −45°. The crystals deposited at −45° were crystallized once more and gave 7.5 gm. of methyl eicosenoate, I.V. 78.7 (theory 78.2). This product was converted to eicosenoic acid, m.p. 23.6°, I.V. 81.0, equiv. wt. 311 (theory 310.5). The acid was hydroxylated by performic acid, giving the low-melting isomer of 11,12-dihydroxyeicosanoic acid, m.p. 96–97°, equiv. wt. 343 (theory 344.5). The melting point was unchanged in admixture with an authentic sample.

The position of the double bond was confirmed by carrying out a cleavage of the dihydroxy acid by periodate. Nonaldehyde (semicarbazone, m.p. 99–100°) and 10-aldehydodecanoic acid (semicarbazone, m.p. 159–160°) were the products. Mixed melting points with pure semicarbazones showed no change.

A second lot of esters was distilled and certain of the C_{18} and C_{22} fractions were examined by low-temperature crystallization. Erucic acid, m.p. 32–34°, was isolated. Esters of saturated acids (C_{16} and C_{18}) were deposited from acetone at −30°. There was little saturated acid in the higher fractions. Dienoic and trienoic acids were determined by ultraviolet spectrophotometry.

The content of eicosenoic acid in the oil is calculated to be about seven per cent of the total fatty acids. Other component acids are estimated as follows: oleic 16, linoleic 25, linolenic 12, erucic 37, saturated acids (mainly palmitic and stearic) 3%.

C. Dogfish Liver Oil

A sample of dogfish liver oil was kindly furnished by the Fisheries Research Board (Canada). It was obtained from dogfish (*Squalus acanthias* L.) taken off the eastern Canadian coast. The oil had I.V. 126, sap. value 165.6, and unsaponifiable matter 13.3%.

It was saponified by potassium hydroxide–ethanol and the unsaponifiable matter was removed by extracting the dried soaps repeatedly with acetone. The soaps were converted to acids and the acids were washed, dried, and esterified. The methyl esters were distilled at reduced pressure (Table III).

Fraction 8, judged to consist mainly of the esters of C_{20} acids, was subjected to repeated crystallization from acetone at temperatures from −30° to −60°. Head and tail fractions were discarded. The purified ester had I.V.

TABLE III
DISTILLATION OF METHYL ESTERS OF DOGFISH LIVER OIL

Fraction	Vapor temp., °C. (approx.)	Wt. of fraction (gm.)	Iodine value
1	110–120	17.3	25.9
2	120–123	19.8	43.9
3	123–127	46.5	44.3
4	127–131	29.6	70.2
5	131–135	38.6	92.8
6	135–137	10.7	94.5
7	137–149	17.0	96.5
8	149–154	26.2	107.6
9	154–162	26.2	109.7
10	162–172	30.0	109.7
R	Residue	55.0	
		316.9	

78.9 (methyl eicosenoate 78.2) and $n_D^{25°}$ 1.4530. It was hydroxylated by performic acid, giving dihydroxyeicosanoic acid (low-melting isomer), m.p. 94–95°, equiv. wt. 345 (theory 344.5). The melting point was not depressed by mixing with authentic 11,12-dihydroxyeicosanoic acid. The content of eicosenoic acid is estimated to be 11% of the total fatty acids.

The lower-boiling esters of dogfish liver oil were examined for hexadecenoic acid. Fraction 1 (Table III), I.V. 25.9, was dissolved in acetone and cooled to −55° to precipitate saturated acids. The filtrate gave 3.0 gm. of esters of I.V. 55.0. This portion was hydroxylated by permanganate and gave an acid of m.p. 123–124°. It did not depress the melting point of a sample of 9,10-dihydroxyhexadecanoic acid, m.p. 124°, prepared in the same way from cod liver oil. The structure of the cod liver oil acid was determined by periodate cleavage and identification of the two fragments.

D. Beluga Oil

A sample of oil from the blubber of the beluga or Hudson Bay white whale (*Delphinapterus leucas* [Pallas]) was obtained from the extraction plant at Churchill, Man.*

The oil had I.V. 116.5, sap. value 210, and unsaponifiable matter 1.4%. It was converted to methyl esters (480 gm.) and distilled at reduced pressure (Table IV). Some low-boiling material, probably methyl isovalerate, was lost at the beginning of the distillation.

It was judged from the course of the distillation that fractions 9 and 10 consisted chiefly of esters of C_{20} acids. They were crystallized three times from acetone, the saturated and polyenoic esters being discarded each time. Two lots of methyl eicosenoate were thus obtained, 4.6 gm. of I.V. 77.9 and 6.7 gm. of I.V. 78.0 (theory 78.2). On saponification and hydroxylation, this material gave dihydroxyeicosanoic acid, m.p. 93–94° (by performic acid) and 128–129° (by alkaline permanganate). These melting points were not

Kindly furnished by W. J. Ward, President, Adanac Whale and Fish Products Ltd.

TABLE IV
DISTILLATION OF METHYL ESTERS OF BELUGA OIL

Fraction	Vapor temp., °C. (approx.)	Wt. of fraction (gm.)	Iodine value
1–4	83–129	225.8	
5	129–132	28.9	95.6
6	132–136	34.0	111.6
7	136–140	38.5	122.2
8	140–146	8.6	139.6
9	146–153	43.3	170
10	153–156	25.3	194
11	156–160	18.6	208
12	160–166	18.3	234
R	Residue	22.3	
		463.6	

depressed on admixture with the low- and high-melting isomers, respectively, of 11,12-dihydroxyeicosanoic acid.

Oxidative cleavage of the dihydroxy acid by sodium periodate gave nonaldehyde (semicarbazone m.p. 94–95°) and 10-aldehydodecanoic acid (semicarbazone m.p. 159–160.5°). Mixed melting points with pure semicarbazones showed no depression.

The quantity of eicosenoic acid originally present in the oil is estimated at 4% of the total fatty acids.

The lower-boiling esters of beluga oil were examined for hexadecenoic acid. Fraction 3 (Table IV), I.V. 82.9, was crystallized from acetone, giving a monoenoic fraction of I.V. 94.5 (methyl hexadecenoate, I.V. 94.6). The yield was poor. It was hydroxylated by permanganate to give dihydroxypalmitic acid, m.p. 123–124°. The melting point was unchanged in admixture with 9,10-dihydroxypalmitic acid made from cod liver oil. The hexadecenoic acid from beluga oil was also converted to the low-melting isomer of 9,10-dihydroxypalmitic acid, m.p. 87–88°.

The data are not sufficient to calculate the content of acids other than eicosenoic. However, the time:temperature distillation curve indicates approximately the following fatty acid groups: below C_{16}, 15%; C_{16}, 40%; C_{18}, 20%; C_{20}, 15%; above C_{20}, 10%.

DISCUSSION

A. Rutabaga seed fatty acids have not been studied hitherto. The constants of the oil and the distillation data show that it is a typical Cruciferae oil, resembling rapeseed oil in composition. The content of eicosenoic acid is similar to that of other Cruciferae.

B. Frenchweed seed fatty acids (*Thlaspi arvense* L.) were described in 1944 in papers by Schrader (5) and by Clopton and Triebold (2). The principal acids were oleic, linoleic, and erucic. The present work shows that there is also an appreciable content of eicosenoic acid. The isolation and purification of 11-eicosenoic acid from this oil was relatively easy.

C. Dogfish liver oil (from *Squalus acanthias* L.) was shown by earlier workers (3) to have a large proportion of C_{20} acids and a lower content of polyenoic

acids than many fish oils. These authors did not isolate the individual acids. However, it is assumed that eicosenoic acid is present in oils of this type. The content of C_{20} acids in our sample of dogfish liver oil is less than the 29% found by Guha and co-workers. The yield of eicosenoic acid was also less than expected. It was difficult to purify, apparently because of the more highly unsaturated acids that accompany it. There was also some difficulty in purifying the derivative, dihydroxyeicosanoic acid, indicating that more than one isomer of eicosenoic acid may be present. This trouble was not encountered in studying the vegetable oils.

D. Beluga oil was examined by Williams and Maslov (6), who analyzed the jaw, head, and body oils separately. They did not report the individual monoenoic acids. The present work shows that 11-eicosenoic acid is present in the oil although in rather small amount, viz. 4% of the total acids. 9-Hexadecenoic acid was also identified and is apparently present in substantial amount.

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THE MASS SPECTRUM OF TITANIUM TETRACHLORIDE[1]

By J. E. Hogg

ABSTRACT

An investigation of the mass spectrum of titanium tetrachloride prepared from both commercial titanium dioxide and titanium minerals has been carried out, using a 180° Nier-type mass spectrometer. Values for the relative abundances of the titanium and chlorine isotopes have been found. Measurements of the singly ionized trichloride group show that any variation in the relative abundances of the isotopes of titanium contained in these samples must be less than one per cent.

INTRODUCTION

Naturally occurring variations have been found in the relative abundances of the non-radiogenic isotopes of many elements, including carbon, oxygen, sulphur, boron, and silicon. The investigations of these variations have been summarized by Thode (6, 7) and Ingerson (3).

Titanium consists of five isotopes of mass numbers 46 to 50. The relatively large mass difference between the lightest and the heaviest of these isotopes might allow natural processes to introduce some fractionation, for it is known from general chemical and physical considerations that the extent of isotopic fractionation is highly dependent on mass differences.

In order to try to detect any major variation in the isotopic abundances of this element, measurements were carried out on samples prepared from commercial titanium dioxide and also from several titanium bearing minerals. These are described in Table I.

TABLE I
DESCRIPTIONS OF SAMPLES ANALYZED

Sample No.	Mineral	Remarks	Location	Source
1	Ilmenite	Beach sand	Melbourne, Florida	Ward's Natural Science Establishment
2	Ilmenite	Massive	Kragero, Norway	Ward's Natural Science Establishment
3	Rutile	Massive	Kragero, Norway	Ward's Natural Science Establishment
4	Rutile	Crystals in feldspar	Pine Creek, N. Carolina	Dr. D. H. Gorman, University of Toronto
5	Rutile	Massive	Unknown	Dr. D. H. Gorman, University of Toronto

The mass spectrometer used in this project was a 180° direction focusing Nier-type instrument with a resolution of 1 mass unit in 300. It has been described in detail by Collins (1). Titanium tetrachloride, a liquid at normal

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temperatures with a high vapor pressure, has suitable properties for analysis by such a spectrometer. A study of the mass spectrum of titanium chloride showed the singly ionized trichloride group to be the most satisfactory for this investigation because it is very abundant, and falls in a mass range which is completely free from any residual hydrocarbon background.

EXPERIMENTAL PROCEDURE

For the production of titanium tetrachloride, a modification of the Dumas method, described by Walton (8), was used. This method involves passing chlorine over an intimate mixture of titanium dioxide and carbon at red heat. The chloride is formed by the reaction:

$$TiO_2 + 2Cl_2 + C \rightarrow TiCl_4 + CO_2.$$

Great care was taken to exclude all moisture from the reaction line, for titanium tetrachloride will react with water vapor. Dissolved chlorine was removed by refluxing in a current of nitrogen. Very high yields can be obtained with the above reaction.

In the preparation of standard samples, C.P. titanium dioxide was used. The mineral samples used included ilmenite ($FeTiO_3$) and rutile (TiO_2) from various mineral associations and from deposits of different ages. Attempts to produce pure titanium tetrachloride from samples of sphene ($CaTiSiO_5$) and pseudobrookite (Fe_2TiO_5) have been unsuccessful.

The first two samples run on the mass spectrometer were prepared from commercial titanium dioxide. These were then mixed together to serve as the standard during the remainder of the runs. A third sample, prepared in the same manner, was run as a check and then discarded.

It was found during preliminary analyses that both the singly and doubly charged ion groups of the tetrachloride, dichloride, and monochloride were formed, as well as singly charged titanium ions. The low mass region of the doubly charged titanium ions was obscured by the spectrometer background, which rises when halogens are introduced through the sample line. The $TiCl_2^{++}$ and $TiCl_4^{+}$ groups were found to be the least abundant. Most abundant were the Ti^{+} and $TiCl_3^{+}$ groups. Because the mass range was slightly obscured up to nearly mass 50, the singly ionized trichloride group was considered to be the most satisfactory for the analyses. An investigation of the mass discrimination introduced by the spectrometer in this range showed it to be much smaller than the precision of the measurements.

The various chlorine and titanium isotopes combine in the formation of titanium trichloride in such a manner as to form ions of 11 masses, from 151 to 161 inclusive. The relative abundances of these were measured with the mass spectrometer. Thus, 11 equations were obtained and solved for the seven unknowns (the abundances of the five isotopes of titanium and the two isotopes of chlorine).

RESULTS

The measured abundances of the components of the $TiCl_3^{+}$ group for each sample analyzed are shown in Table II. Using five of the equations mentioned

TABLE II

PEAK HEIGHTS OF THE TITANIUM TRICHLORIDE GROUP FROM ANALYSES OF SAMPLES AND STANDARDS

Sample	Peak heights of masses observed										
	151	152	153	154	155	156	157	158	159	160	161
Std. A	3.40	3.13	35.05	5.43	34.37	3.31	12.46	0.858	1.819	0.080	0.080
Std. B	3.40	3.14	35.09	5.43	34.35	3.30	12.45	0.856	1.820	0.081	0.080
Std. C	3.43	3.14	35.16	5.45	34.30	3.30	12.40	0.855	1.812	0.078	0.076
Std. A+B	3.40	3.13	35.05	5.42	34.39	3.31	12.46	0.864	1.816	0.076	0.077
No. 4	3.42	3.14	35.11	5.41	34.41	3.29	12.45	0.850	1.808	0.074	0.072
No. 4	3.41	3.12	35.12	5.42	34.37	3.30	12.45	0.851	1.818	0.074	0.074
No. 2	3.40	3.14	35.11	5.42	34.37	3.29	12.45	0.849	1.817	0.074	0.074
Std. A+B	3.43	3.14	35.16	5.45	34.30	3.30	12.43	0.848	1.810	0.072	0.073
No. 3	3.42	3.13	35.10	5.44	34.33	3.30	12.46	0.851	1.820	0.076	0.077
No. 1	3.42	3.15	35.14	5.43	34.36	3.32	12.41	0.854	1.813	0.072	0.072
Std. A+B	3.41	3.15	35.12	5.44	34.34	3.31	12.43	0.849	1.818	0.072	0.071
Std. A+B	3.42	3.14	35.14	5.45	34.35	3.29	12.41	0.850	1.805	0.074	0.075
No. 2	3.41	3.13	35.11	5.40	34.41	3.31	12.43	0.853	1.803	0.074	0.073
No. 5	3.42	3.14	35.13	5.41	34.41	3.29	12.42	0.848	1.803	0.071	0.073
No. 1	3.40	3.12	35.10	5.42	34.41	3.30	12.44	0.849	1.815	0.072	0.071
Std. A+B	3.42	3.13	35.11	5.43	34.41	3.29	12.41	0.847	1.807	0.073	0.073
Std. A+B	3.40	3.12	35.16	5.43	34.41	3.29	12.38	0.852	1.814	0.080	0.079
No. 3	3.40	3.14	35.17	5.39	34.38	3.28	12.43	0.848	1.807	0.077	0.073
No. 5	3.42	3.14	35.11	5.40	34.35	3.30	12.46	0.852	1.813	0.075	0.075
Std. A+B	3.42	3.13	35.11	5.43	34.41	3.29	12.41	0.847	1.807	0.073	0.073
Std. A+B	3.40	3.12	35.15	5.42	34.41	3.28	12.42	0.849	1.803	0.074	0.075

Note: The analyses are listed in the order in which they were made.

TABLE III

ISOTOPIC ABUNDANCES OF TITANIUM SAMPLES

Sample	Per cent abundance				
	Ti^{46}	Ti^{47}	Ti^{48}	Ti^{49}	Ti^{50}
Std. A	7.96	7.31	73.89	5.50	5.34
Std. B	7.96	7.33	73.91	5.47	5.32
Std. C	8.03	7.34	73.93	5.48	5.22
Std. A+B	7.96	7.30	73.93	5.50	5.32
No. 4	8.00	7.33	74.03	5.43	5.25
No. 4	7.98	7.29	73.98	5.47	5.29
No. 2	7.96	7.33	73.99	5.44	5.29
Std. A+B	8.03	7.34	73.95	5.46	5.23
No. 3	8.01	7.32	73.88	5.47	5.33
No. 1	8.00	7.34	73.99	5.47	5.23
Std. A+B	7.98	7.36	73.95	5.46	5.27
Std. A+B	8.00	7.34	74.01	5.45	5.20
No. 2	7.98	7.30	74.06	5.47	5.21
No. 5	8.00	7.33	74.07	5.43	5.20
No. 1	7.96	7.29	74.03	5.46	5.27
Std. A+B	8.00	7.32	74.03	5.44	5.22
Std. A+B	7.96	7.29	74.05	5.47	5.23
No. 3	7.96	7.33	74.11	5.41	5.20
No. 5	8.00	7.32	73.94	5.45	5.28
Std. A+B	8.00	7.32	74.02	5.44	5.23
Std. A+B	7.96	7.29	74.13	5.44	5.18
Average	7.99	7.32	73.99	5.46	5.25
Std. Deviation	0.02	0.02	0.07	0.02	0.05

Note: The analyses are listed in the order in which they were made.

above, values for the relative abundances of the titanium isotopes were obtained by assuming various values for the Cl^{37}/Cl^{35} ratio. These values were then substituted in the six remaining equations in order to calculate the corresponding $TiCl_3^+$ abundances. By comparison of these values with the measured ones, it was found that $Cl^{37}/Cl^{35} = 246/754$, the values obtained by Nier (5), gave the best result, values one per cent on either side of this giving large discrepancies between the observed and the calculated $TiCl_3$ peak heights.

Using this value for the relative abundances of the chlorine isotopes, the 11 equations were solved by a method of least squares for the abundances of the five titanium isotopes. The results are shown in Table III.

CONCLUSIONS

Among the samples analyzed no significant variations in the relative abundances of the titanium isotopes were found. Small systematic errors were too small to be significant. The average of these abundances is given in Table IV, along with the values obtained by Nier (4) and Hibbs (2). It is seen that the author's determinations result in a slightly greater abundance of Ti^{48} than that obtained by Nier or Hibbs. No explanation has been found for this difference.

TABLE IV
SUMMARY OF THE RELATIVE ABUNDANCES OF THE TITANIUM ISOTOPES

	Author	Nier	Hibbs
Ti^{46}	7.99	7.95	8.22
Ti^{47}	7.32	7.75	7.42
Ti^{48}	73.99	73.45	73.38
Ti^{49}	5.46	5.51	5.56
Ti^{50}	5.25	5.34	5.41

In order to study the isotopes of titanium with a gas source mass spectrometer, the sample must be introduced as a halide. Using titanium tetrachloride, it was found that HCl was unavoidably produced in the spectrometer, and that this compound can only be removed from the spectrometer tube by very long periods of baking out at high temperatures. Solid compounds, which formed a coating on the inside of the tube, were also produced. In addition, it is possible that the chemical procedures carried out may have introduced isotopic fractionation, since the use of volatile compounds was involved. The properties of titanium tetrafluoride and tetrabromide are such as to render these compounds even less satisfactory for mass spectrometeric analysis.

Because of these disadvantages in the use of the halides of titanium, a solid source mass spectrometer might give measurements of the relative abundances of the titanium isotopes of greater precision than those reported here. With this type of instrument, the samples might be introduced as titanium dioxide, the form in which the element usually occurs in nature.

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NOTE

THE RAMAN SPECTRA OF TRICHLOROETHYLENE: C_2HCl_3 AND C_2DCl_3*

BY G. ALLEN† AND H. J. BERNSTEIN

The infrared spectra of light and heavy trichloroethylene have been reported by Bernstein (1) together with a summary of previous Raman investigations on the light compound. The assignment for CHCl=CCl_2 has since been revised on the basis of the sum rule for vibrational frequencies (2), but no depolarization data were available to confirm the new assignment. No Raman spectrum has been reported for CDCl=CCl_2. In this investigation the Raman spectra and depolarization data have been obtained for both compounds and the revised assignment (2) for CHCl=CCl_2 has been confirmed. The assignment for CDCl=CCl_2 has also been revised.

EXPERIMENTAL

The Raman spectra of pure CHCl=CCl_2 and CDCl=CCl_2 diluted with CCl_4 have been obtained on a photoelectrically recording spectrometer (5).

TABLE I
RAMAN SPECTRA[a]

		CHCl=CCl_2		CDCl=CCl_2	
	Approx. character	Wave numbers	Depolarization ratio	Wave numbers	Depolarization ratio
ν_1	ν CH	3080(s)	0.31	2302(s)	0.36
ν_2	ν C=C	1589(s)	0.40	1589(m)[b] 1561(s)[b]	0.46 0.40
ν_3	δ CH	1242(m)	0.56	1014(m)	0.51
ν_4	ν CCl	932(w)	0.65	876(w)	P?
ν_5	ν CCl	840(w)	0.24	792(m)	0.35
ν_6	ν CCl	628(s)	0.16	618(s)	0.27
ν_7		381(s)	0.35	381(s)	0.33
ν_8	δ skeletal	274(s)	0.77	274(s)	0.80
ν_9		172(s)	0.60	172(s)	0.60
ν_{10}	δ CH	780(m)	0.87	630(m)	0.87
ν_{11}		450(m)	0.87	427(m)	0.87
ν_{12}	δ skeletal	211(m)	0.87	213(m)	0.87
$2 \times \nu_{11}$		907(v.w.)			
$2 \times \nu_8$		530(v.w.)		530(v.w.)	

[a]*Although the numbering of fundamentals (ν_1 etc.) is still identified with the schematic representation of the vibrational modes given by Bernstein (Fig. 5, Ref. 1), the assignment is different from that given in Table I of Ref. 1.*

[b]*Resonance doublet, with fundamental in the region $\backsim 1570$ cm^{-1}.*

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†*National Research Council Postdoctorate Fellow 1952–54.*

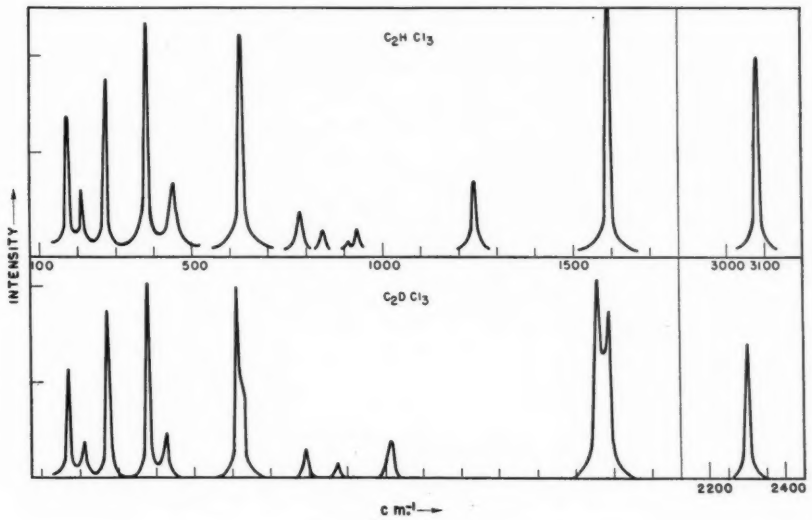

FIG. 1

Depolarization ratios were obtained by the method of Edsall and Wilson (3) and corrected for convergence (4). The results are given in Table I and Fig. 1.

DISCUSSION

Since three antisymmetrical out-of-plane vibrational modes are expected, these are assigned to the three depolarized bands in each spectrum. The in-plane or symmetrical modes can then be assigned as shown in Table I. The assignment for $CHCl{=}Cl_2$ is now identical with the one indicated by the sum rule (2); the major difference between the present and original (1) assignments is that the band at 932 cm.$^{-1}$ is now assigned as an in-plane mode whereas the band at 450 cm.$^{-1}$ is now assigned as an out-of-plane mode. The assignment for $CDCl{=}CCl_2$ has been revised in a similar manner to make it consistent with that for the light compound.

The two assignments are consistent with the Bernstein–Pullin (2) sum rule for isotopic substitution. The rule predicts

$$\text{out-of-plane} \quad \sum \nu C_2HCl_3 - \sum \nu C_2DCl_3 = 173 \text{ cm.}^{-1}$$

$$\text{in-plane} \quad \sum \nu C_2HCl_3 - \sum \nu C_2DCl_3 = 1095 \text{ cm.}^{-1}$$

and the observed differences are 173 and 1105 cm.$^{-1}$ respectively.

Thermodynamic Functions

The functions given in Table II were calculated for $CHCl{=}CCl_2$ by the usual statistical methods using the wave numbers of fundamentals as given in Table I. The following structural parameters were used to calculate the

TABLE II
THERMODYNAMIC FUNCTIONS FOR $CHCl{=}CCl_2$
(Units cal. deg.$^{-1}$ mole^{-1})

T, °K.	$C°_P$	$\frac{H° - E°_0}{T}$	$\frac{-F° - E°_0}{T}$	$S°$
298.16	19.172	13.333	64.296	77.629
300	19.245	13.370	64.377	77.747
400	21.795	15.172	68.476	83.648
500	23.669	16.693	72.031	88.724
600	25.063	17.978	75.191	93.169
700	26.115	19.066	78.042	97.108
800	26.942	20.001	80.650	100.651
900	27.605	20.812	83.062	103.874
1000	28.145	21.519	85.284	106.803
1100	28.594	22.144	87.376	109.520
1200	28.964	22.692	89.311	112.003
1300	29.283	23.191	91.155	114.346
1400	29.551	23.633	92.884	116.517
1500	29.783	24.040	94.544	118.584

product of the principal moments of inertia:

$$C{-}H = 1.08\ \text{Å}, \quad C{=}C = 1.36\ \text{Å}, \quad C{-}Cl = 1.72\ \text{Å};$$
$$\angle CCH = 120°, \quad \angle HCCl = 116°, \quad \angle ClCCl = 117°.$$

The product of the three principal moments is calculated to be 9.05×10^{-113} c.g.s. units.

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